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THE CONCURRENT REARRANGEMENT AND SUBSTITUTION
OF TRITYL ARENESULFINATES

BY

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A THESIS

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The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled, "The Concurrent Rearrangement and Substitution of Trityl 2-methyl-benzenesulfinate", submitted by Hendrick H. Persad in partial fulfillment of the requirements for the degree of Doctor of Philosophy.



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ABSTRACT

The reaction of trityl 2-methylbenzenesulfinate was examined in both solvents chloroform and acetonitrile. In the former solvent in the presence of tetrabutylammonium benzoate or p-nitrobenzoate the principle reaction appears to be rearrangement accompanied by a variable degree of substitution depending on the quaternary ammonium salt concentration. Trityl 2-methylbenzenesulfinate reacts 10^4 times faster than benzyl 2-methylbenzenesulfinate with tetrabutylammonium azide in chloroform. The expected mode of reaction of benzyl 2-methylbenzenesulfinate under these conditions is attack of azide ion on the primary carbon displacing the arenesulfinate function. It was concluded that the substitution reaction of trityl 2-methylbenzenesulfinate under analogous conditions involves an ion pair exchange reaction.

In acetonitrile trityl 2-methylbenzenesulfinate rearranges to trityl 2-methylphenyl sulfone. In the presence of tetrabutylammonium azide a portion of the product sulfone is diverted to trityl azide, indicating the presence of two distinct ionic species, one non-capturable which is not easily diverted to trityl azide and the other a trappable species capable of facile diversion to trityl azide. It was not possible to determine the nature of these species from the results of the reaction of trityl 2-methylbenzenesulfinate.

Trityl 2,6-dimethylbenzenesulfinate does not rearrange to trityl 2,6-dimethylphenyl sulfone but does undergo exchange reactions with added nucleophiles. Common ion rate depression was observed in the reaction of

this ester with tetrabutylammonium azide and 2,6-dimethylbenzenesulfinate in acetonitrile under conditions analogous to the reaction of trityl 2-methylbenzenesulfinate. Due to the close structural similarity between these two esters, it was concluded that in the concurrent rearrangement and substitution of trityl 2-methylbenzenesulfinate in acetonitrile that a dissociated trityl cation is the capturable species.

Competition experiments were carried out by allowing trityl perchlorate and trityl 2-methylbenzenesulfinate to react with tetrabutylammonium azide and 2,6-dimethylbenzenesulfinate in acetonitrile, and these results are also given.

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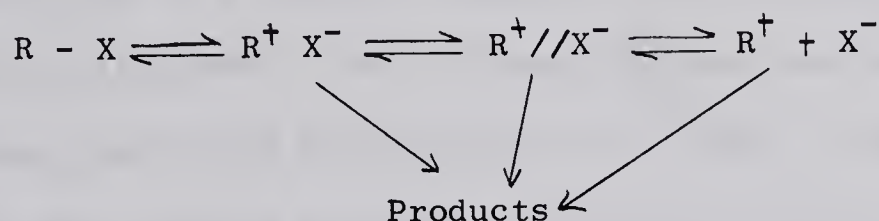
INTRODUCTION

The study of solvolysis reactions has been one of the most important areas of research in the field of physical-organic chemistry. Many solvolysis reactions have been shown to involve carbonium ion intermediates, resulting often in products with partial net inversion of configuration (32). Racemic solvolysis products should be formed if dissociated ions are the only intermediates formed. Hammett (29) in 1940 suggested the intervention of ion pairs to explain the partially inverted configuration of α -phenylethyl acetate formed during the acetolysis of α -phenylethyl bromide.

Young, Winstein and Goering (30) presented the first compelling evidence, indicating the importance of ion pairs as intermediates in solvolysis reactions. In the acetolysis of α,α -dimethylallyl chloride, solvolysis is accompanied by a concurrent rearrangement to γ,γ -dimethylallyl chloride. The instantaneous first-order rate constants for acetolysis of the tertiary halide decreased from ca. $15 \times 10^{-6} \text{ sec.}^{-1}$, to ca. $2.2 \times 10^{-6} \text{ sec.}^{-1}$, by the time the reaction is 30% complete, thereafter remaining constant. This latter value is the rate constant for the solvolysis of the primary isomer. If solvolysis of the initially pure α,α -dimethylallyl chloride was stopped after 30% reaction, γ,γ -dimethylallyl chloride was the only isolable allylic chloride. No common ion rate depression was observed on addition of chloride ion. Therefore a free carbonium ion is not returning to the primary isomer by reacting with external chloride ion. On the basis of these results, it

was suggested that the allylic rearrangement of α, α -dimethylallyl chloride to γ, γ -dimethylallyl chloride took place by "internal return", from an ion pair intermediate. Since then considerable further evidence has been accumulated on the importance of ion pairs in solvolysis and rearrangement reactions.

Extensive study of solvolysis reactions by Winstein and his co-workers (35) has enabled these authors to propose a scheme in which two different ion pair species are defined.



Products may be formed from any or all of the intermediates as is shown in the above scheme. $R^+ X^-$ is an "intimate ion pair", made up of a carbonium ion and anion essentially in contact. $R^+ // X^-$ is the "external" or "solvent separated" ion pair, where the two oppositely charged entities are separated by a small number of solvent molecules. The ions are held together as one unit in the solvent by electrostatic attraction. $R^+ + X^-$ represents dissociated ions in which each ion acts as a completely independent particle.

These workers suggested that return of carbonium ion intermediates to covalent RX may occur from the dissociated carbonium ion stage, which they termed "external ion return", or from ion pairs, "ion pair return" (33).

Ion pair return may be further dissected into return from the intimate ion pair, "internal return", and return from the solvent-separated ion pair, "external ion pair return", (33, 34).

In the acetolysis of threo-3-p-anisyl-2-butyl p-bromobenzene-sulfonate at 25⁰, the polarimetric rate constant is greater than the titrimetric rate constant by a factor of four (34). The reaction does not involve dissociated ions, since addition of p-bromobenzenesulfonate did not give rise to common ion rate depression. Addition of lithium perchlorate gave rise to a linear increase in the polarimetric rate constant termed a "normal salt effect". The titrimetric rate constant under the same conditions, exhibited a steep rise up to about 0.03 M salt concentration, (special salt effect) followed by a linear increase at higher lithium perchlorate concentrations. When the linear portion of the curve is extrapolated to zero salt concentration, the intercept, $k_0(\text{ext.})$, is about 2.6 times the observed titrimetric rate constant in the absence of salt. At no salt concentration is the titrimetric rate constant equal to the polarimetric rate constant. These results are illustrated in Figure I.

Ionization of the substrate would be expected to yield the symmetrically bridged ion, hence the rate of ionization is measured by the polarimetric rate. Since the steep rise in rate on addition of lithium perchlorate affects only the titrimetric rate constants and not the polarimetric rate constants, it cannot be an ionic strength phenomenon on the ionization rate, and must be concerned with the reactions subsequent to ionization of ion pairs once they are formed. The absence of common

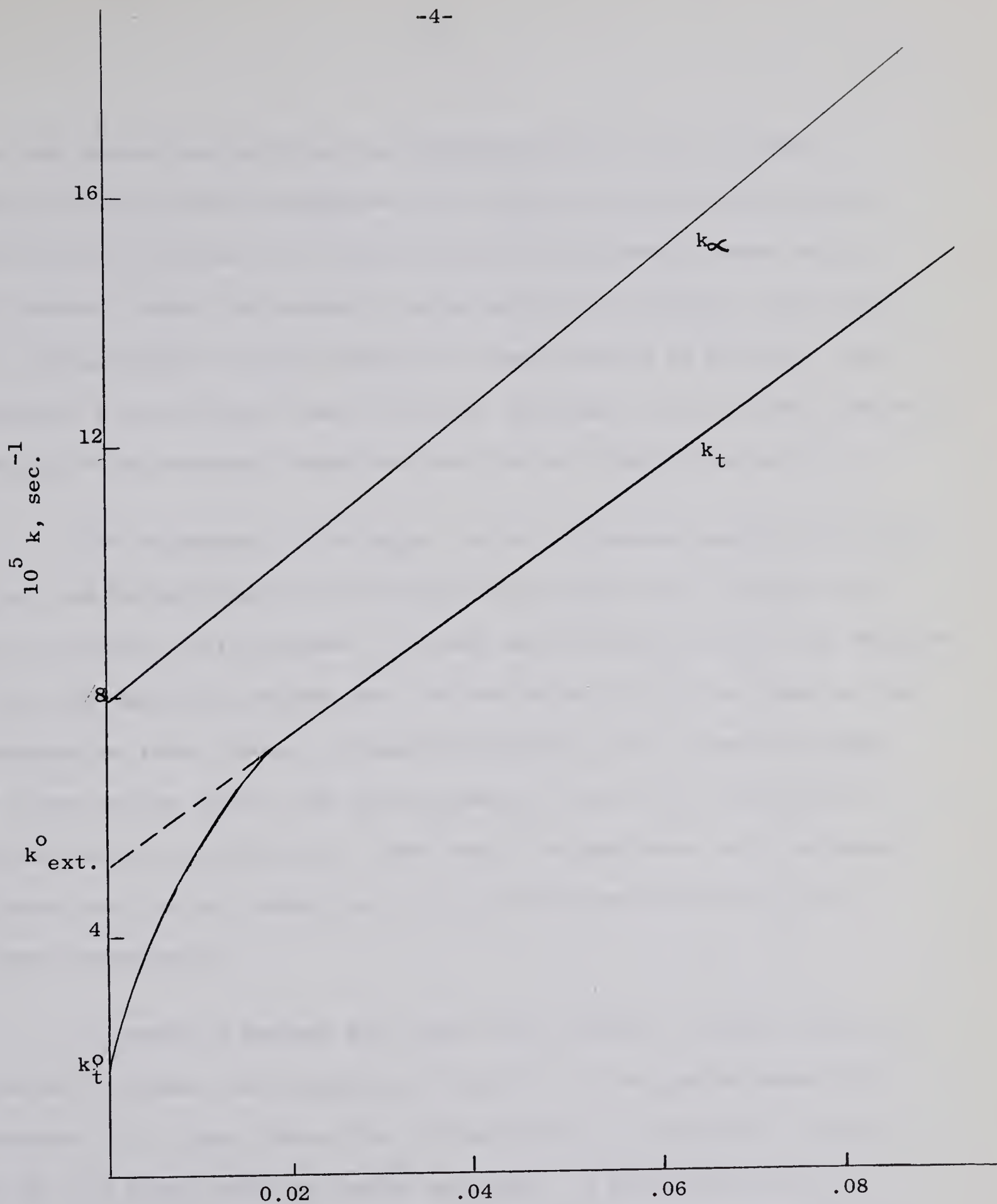


Figure I

$(\text{LiClO}_4), \text{M}$

Effect of lithium perchlorate on acetolysis of threo-3-p-anisyl-2-butyl p-bromobenzenesulfonate at 25° (taken from S. Winstein and G.C. Robinson, J. Am. Chem. Soc., 80, 169 (1958)).

ion rate depression indicates that dissociated ions are not formed. Winstein and co-workers suggested that lithium perchlorate intercepted an ion pair diverting it to a new species $R^+//ClO_4^-$ which cannot return to covalent product and rapidly yields solvolysis products. Since after all the capturable ion pair species has been diverted to $R^+//ClO_4^-$ racemization is still faster than solvolysis there must also be a non capturable species in the reaction. Hence the need for two types of ion pairs.

The importance of ion pairs in the solvolysis reactions described above, was demonstrated with substrates which gave rise to bridged ions and to certain allylic systems. In cases where symmetrical ions are produced it may reasonably be assumed that the ionization rate is the same as the racemization rate. However in open chain systems, the intimate ion pair $R^+ X^-$ may not be racemic and the polarimetric rate is not necessarily a measure of the ionization rate. The rate of racemization would represent a lower limit of the ionization rate, since ion pair return may occur without racemization.

A number of methods have been used to detect ion pair return in open chain systems. Racemization of optically active p-chlorobenzhydryl chloride is 2.5 times faster than its solvolysis in 80% aqueous acetone and 30 - 70 times faster in acetic acid (38). In 80% acetone the racemization rate constant is greater by a factor of two than the sum of the rate constants for solvolysis and exchange with $^{36}Cl^-$. Since the exchange reaction is a measure of maximum return from dissociated ions, it follows that the racemization occurs without the formation of dissociated ions,

and must involve ion pair return. In the reaction of benzhydryl p-nitrobenzoate carbonyl- ^{18}O in 90% aqueous acetone, Goering and co-workers (40) found that exchange of ^{18}O between carbonyl and ether oxygens is three times faster than solvolysis. The intramolecular equilibration accompanying solvolysis involves ion pair return.

Additional evidence has been presented by Goering and co-workers (41) for the existence of two distinct types of ion pairs. During the solvolysis of optically active p-chlorobenzhydryl p-nitrobenzoate carbonyl- ^{18}O in 80 and 90% aqueous dioxane, both racemization and scrambling of the ^{18}O occurs. When the reaction is carried out in the presence of 0.14 M sodium azide racemization is completely eliminated, while scrambling of the ^{18}O label still takes place. Since both these reactions were shown to be at least 99% intramolecular, two types of ion pairs must be present, return from one giving rise to both randomization and racemization, while return from the other gives randomization only.

Ion pair return has been postulated in certain systems where recombination of ion pairs may lead to a stable product which is isomeric with the starting material. Smith (42) in studying the solvolysis of benzhydryl thionbenzoate in ethanol found that 83% benzhydryl thiolbenzoate and 17% benzhydryl ethyl ether are formed. The relative rates of reaction of p-methylbenzhydryl thionbenzoate and p-chlorobenzhydryl thionbenzoate compared to benzhydryl thionbenzoate are 17 and 0.53 respectively. A

ρ value (63) of -3.6 was obtained, a value typical of ionization reactions of benzhydryl compounds. When equimolar concentrations of potassium-p-

methoxythionbenzoate and benzhydryl thionbenzoate were allowed to react in ethanol no benzhydryl-p-methoxythiolbenzoate was formed. The absence of exchange indicates that dissociated ions are unimportant for the formation of rearranged products. Therefore at least 83% of the reaction proceeds by ion pairs. It was similarly shown that in solvents up to the polarity of acetonitrile, benzhydryl thiocyanate rearranges to benzhydryl isothiocyanate mainly by ion pair return (43).

The nature of the rearrangement of arenesulfinates to sulfones has been of interest to a number of workers. Some evidence in the literature discussed below indicated that the sulfinates-sulfone rearrangement reaction could occur by ion pair return.

Analogous to carboxylate esters, where alkyl-oxygen or acyl-oxygen bond cleavage may take place during reaction, the solvolysis of arenesulfinates may proceed by sulfur-oxygen bond fission or carbon-oxygen bond fission. The extent to which each of the above processes will take place, depends on the structure of the ester and the reaction conditions used. Darwish and Noreyko (44) have presented a discussion on sulfur-oxygen bond fission, and since the present work is concerned with ionization, only those systems in which the results are consistent with carbon-oxygen bond breaking will be discussed.

In the solvolysis of optically active arenesulfinates, racemization may take place on ion pair return in a manner similar to that observed with chlorides. In addition, ion pair return in arene-

sulfinate esters may be accompanied by the formation of a new compound a sulfone, isomeric with the starting material and usually stable under the reaction conditions (44).

Kenyon, Phillips and co-workers (46, 47) observed that optically active α -phenylethyl p-toluenesulfinate on standing at room temperature for several days decomposed to give among other products racemic α -phenylethyl p-tolyl sulfone (46). Solvolysis of the above ester in acetic acid resulted in the production of racemic α -phenylethyl acetate and a little racemic α -phenylethyl 4-methylphenyl sulfone (47). When the solvolysis is carried out in ethanol the corresponding ethyl ether of slightly inverted configuration is formed. In contrast if the ethanolysis is carried out in the presence of potassium carbonate, α -phenylethanol was formed with complete retention of configuration. The formation of completely retained α -phenylethanol is consistent with sulfur-oxygen bond cleavage rather than carbon-oxygen bond cleavage. The formation of racemic α -phenylethyl acetate and α -phenylethyl p-tolyl sulfone is consistent with carbon-oxygen bond cleavage. α -Phenylethyl ethyl ether of inverted configuration also must be formed by carbon-oxygen bond cleavage.

The ethanolysis of the optically active p-toluenesulfinate of ethyl 3-hydroxy-3-phenylpropionate resulted in the corresponding ethyl ether of partially inverted configuration (48). When potassium carbonate was added under the same conditions the corresponding alcohol of completely retained configuration was formed. The results indicated that in the absence of potassium carbonate carbon-oxygen bond cleavage took place.

The formation of ethyl 3-hydroxy -3-phenylpropionate during ethanolysis in the presence of potassium carbonate is proof that sulfur-oxygen bond cleavage has taken place.

In a later publication additional evidence on the solvolysis of optically active α -phenylethyl p-toluenesulfinate was presented (49). In formic acid a 60% yield of purified racemic sulfone was isolated. In formic acid containing sodium formate solvolysis of the ester resulted in the isolation of only 10% of purified sulfone. However the sulfone was formed with about 63% net retention of configuration. The α -phenylethyl formate isolated in the above reaction was also of partially retained configuration indicating that sulfur-oxygen bond cleavage was also taking place under these conditions. Keyon suggested that racemic sulfone was formed by an ionic mechanism and retained sulfone by a non-ionic rearrangement. Streitwieser (50), suggested that an alternative explanation would be that retained sulfone is formed by ion pair return.

Cope and co-workers (51) in studying the rearrangement of γ -methylallyl benzenesulfinate and α -methylallyl benzenesulfinate in toluene at 100°C, in each case isolated γ -methylallyl phenyl sulfone. They suggested three possible pathways to sulfone formation, one of which involved an ionic mechanism. The other two pathways to sulfone formation suggested were (i) an allylic rearrangement to give a mixture of two sulfinates followed by another rearrangement to give sulfone and, (iii) an allylic rearrangement to give sulfone followed by formation of an equilibrium mixture of the two possible sulfones.

Wragg, McFadyen and Stevens (52) found that benzhydryl p-toluenesulfinate rearranged to the corresponding sulfone in acetic acid and nitromethane but not in acetonitrile, benzene or toluene. In the last three solvents however reaction did occur in the presence of p-toluenesulfinic acid. In acetic acid in the presence of p-chlorobenzenesulfinic acid some benzhydryl p-chlorophenyl sulfone was isolated. The rates of rearrangement of the homogeneous p-toluene sulfates were found to be in the following order: o-methylbenzhydryl > benzhydryl > α -phenylethyl. Benzhydryl p-chlorobenzenesulfinate was also found to react faster than benzhydryl p-toluenesulfinate. The above order is consistent with a rate determining ionization. The fact that exchange was observed in the formation of sulfone is also consistent with an ionization process.

McLaren (53) has reported the results of the reaction of α -phenylethyl and α -(p-methoxyphenyl)ethyl 2,6-dimethylbenzenesulfinate in ethanol and aqueous ethanol. The rate of rearrangement of the latter in ethanol is four to five powers of ten faster than the former. This substituent effect is of the order expected for an ionic reaction. Both the solvolysis and rearrangement reactions showed sensitivities to changes in solvent, and the presence of salts, consistent with an ionic mechanism. For both esters no common ion rate depression was observed and the yield of sulfone is unaffected by the presence of added 2,6-dimethylbenzenesulfinate ion. Under comparable conditions α -phenylethyl bromide in the presence of 2,6-dimethylbenzenesulfinate ion yielded less than 0.4% α -phenylethyl 2,6-dimethylphenyl sulfone. α -(p-Methoxyphenyl)ethyl bromide under the same conditions gave rise to less than 0.7% α -(p-methoxyphenyl)ethyl 2,6-dimethylphenyl

sulfone. These results are consistent with an ionic intramolecular mechanism of sulfone formation. Ion pair return has thus been detected by the sulfinates-sulfone rearrangement.

Mermelstein (54) has shown that the principal mode of reaction of a number of 2-aryl-2-propyl 2,6-dimethylbenzenesulfinates in a variety of hydroxylic solvents, is solvolysis accompanied by rearrangement to the corresponding sulfones. Substituent effects and the almost equal sensitivity to changes in ionizing power of the solvent for both solvolysis and rearrangement established an ionic mechanism to be operative. For both 2-phenyl-2-propyl and 2-p-methoxyphenyl-2-propyl 2,6-dimethylbenzenesulfinates no common ion rate depression was observed. The yield of sulfone is unaffected by the addition of 2,6-dimethylbenzenesulfinate ion. These results are consistent with an ionic intramolecular rearrangement for sulfone formation, involving ion pair return.

The exceptional stability associated with the trityl cation have interested organic chemists for a long time. But while the physical and chemical properties of derivatives of these systems have been widely investigated it was not until very recently that attempts were made to estimate for trityl systems the importance of ion pairs and ion pair return. Compared to other systems that undergo ionization to produce carbonium ion intermediates during solvolysis and other reactions, trityl systems represent rather a structural extreme and could provide an important calibration point for the understanding of ion pairs and dissociated ions.

Most of the early work on triarylcarbonium ions related to conductivity experiments which served to establish the ready ability of triaryl derivatives to ionize, which characteristic is due to the stability of the triarylcarbonium ion.

The conductivity studies of Walden (1) and Gomberg (2) showed that triarylmethyl halides ionize in sulfur dioxide, and that solutions of these compounds were comparable to those of ionic substances such as methylammonium chloride and potassium iodide which are strong electrolytes in sulfur dioxide. Conductivity studies in sulfur dioxide by later workers (3, 4, 5) showed the effect of substituents on the ionization. The substituted trityl chlorides gave conductivity curves in sulfur dioxide that showed a definite dependence on the nature of the substituents.

Lichtin and Bartlett (6) and Lichtin and Glazer (7) carried out conductivity measurements to study the effect of the substituent on ionization for a series of triarylmethyl chlorides in sulfur dioxide at 0°. They determined the effect of changes in structure on the extent of ionization. Trityl chloride and tris-p-tertiarybutylphenylmethyl chloride were studied at -17° and 0°, therefore allowing the determinations of enthalpies and entropies of ionization in sulfur dioxide. For trityl chloride at 0° in sulfur dioxide the experimental dissociation constant obtained was 4.03×10^{-5} . The values obtained for the other constants were; $\Delta F^\circ = +5.49$ kcal./mole, $\Delta H = -8.9$ kcal./mole, and $\Delta S^\circ = -53$ cal./mole. For tris-p-tertiarybutylphenylmethyl chloride, the values obtained were, $K = 800 \times 10^{-5}$, $\Delta F^\circ = +2.62$ kcal/mole, $\Delta H = 1.8$ kcal/

mole, and $\Delta S^\circ = -17$ cal./mole. Although the net effect of the tertiary butyl substituent is to increase the degree of ionization by lowering ΔF° marked changes on ΔH and ΔS° occur and these are in opposite directions.

Conductivity gives a measure of the free ions present under a particular set of conditions, but tells nothing of the concentration of ion pairs or ion aggregates that may be present under these conditions. This difficulty may be overcome by the use of spectrophotometry, and various chemical techniques, both of which have been effectively employed to determine the types and concentrations of the different ionic species present.

Ultraviolet spectrophotometry, measures both the free ions and ion pairs. Data from this source in conjunction with conductivity results can lead to the determination of the relative concentrations of ion pairs or dissociated ions present (72). This form of investigation is applicable to the trityl system, because of the intense yellowish-red coloration characteristic of the ion.

A large percentage of the work on the trityl system within the last sixteen years has been conducted with trityl chloride and both ultraviolet spectrophotometry and kinetic methods have been used to determine equilibrium constants and reaction processes (8 - 25). There has been much controversy associated with these investigations.

The values of the equilibrium constants K_1 and K_2 for the ionization of trityl chloride to ion pairs and dissociated ions in nitromethane solvent were reported by Evans (8, 10). Leffler and co-workers (9) reported their inability to reproduce Evans' results while Smith and Rao (11) acknowledged the accuracy and reproducibility of the same results.

The mechanism of solvolysis and nucleophilic substitution of trityl chloride in solvents of low dielectric constants has been studied extensively (13 - 25). Ingold and co-workers (23) reported and discussed the rates of nucleophilic substitution of trityl chloride in benzene solvent by small concentrations of methanol, tetrabutylammonium azide and radio-chloride. C.G. Swain and co-workers (16, 20), also studied the reactions of trityl chloride in benzene. So far there has only been one area in which both schools of thought agree, and that is in the substitution and solvolysis of trityl chloride, attack by the nucleophile occurs on the carbonium ion of an ion pair intermediate. Winstein (25) has pointed out that with benzene as solvent trityl chloride is a poor choice as substrate not only because of the experimental difficulties involved, but also because there is no way of estimating the ionization rate constants, and therefore no indication of the magnitude of ion pair return during methanolysis or exchange.

Swain and Tsuchihashi (57) reported a first-order rate constant of $3.8 \times 10^{-6} \text{ sec}^{-1}$, for ^{18}O equilibration for carbonyl- ^{18}O -labeled trityl benzoate in dry acetone at 60° . With 0.020 M trityl benzoate carbonyl- ^{18}O

and 0.006 M lithium azide, the initial rate of equilibration dropped to zero. First-order rate constants from following the disappearance of azide ion were $4.4 \pm 0.4 \times 10^{-6} \text{ sec.}^{-1}$, and $6.3 \times 10^{-6} \text{ sec.}^{-1}$, with 0.006 and 0.010 M lithium azide, respectively. Trityl azide was isolated in 95% yield from the reaction with 0.02 M lithium azide. The azide capture rate is only slightly larger than the ionization rate of trityl benzoate. This was attributed to a salt effect of lithium azide. These results were interpreted in terms of one ion pair visualized as $(\text{C}_6\text{H}_5)_3\text{C}^+-\text{O}_2\text{CC}_6\text{H}_5$, termed an "ordinary ion pair", which is the capturable intermediate in this rearrangement, distinct from covalent substrate, and that it is the same intermediate as for substitution by lithium azide. Swain suggested that earlier (more intimate) partly or totally equilibrated ion pairs were not required to explain the results, since rearrangement was completely suppressed early in the reaction.

Winstein and Appel (73) have reported additional results on the ^{18}O equilibration reaction of trityl benzoate-carbonyl- ^{18}O in dry and moist acetone. The results contrast markedly with those reported by Swain and Tuschihashi (57). The first-order rate constant (k_{eq}) for carbonyl- ^{18}O equilibration reported by Winstein and Appel is $46 \times 10^{-7} \text{ sec.}^{-1}$, in anhydrous acetone at 75.0° . First-order rate constants (k_e) for exchange with tetrabutylammonium carbonyl- ^{14}C -labeled benzoate are much smaller but increased as the concentration of the salt increased. It was also shown that first-order rate constants (k_{N_3}) for consumption of azide ion from added tetrabutylammonium azide are equal to k_e values with tetrabutylammonium benzoate, and that neither k_{N_3} or k_e depended on the concent-

ration of nucleophile. The addition of tetrabutylammonium azide did not suppress equilibration of ^{18}O , but it did suppress exchange. The azide/benzoate competition factor obtained was ca. 2. If k_{eq} or $(k_{\text{eq}} + k_{\text{N}_3})$ is taken as an estimate of the ionization rate constant then ionization rates exceed chemical capture rates by factors of 40 down to ca. 13 depending on the tetrabutylammonium salt concentration. It was suggested that ^{18}O equilibration proceeds by way of an ion pair intermediate not capable of facile diversion to exchange products. However added nucleophiles do compete for and trap very efficiently one or more further intermediates.

The results reported by Winstein and Appel are qualitatively similar to that observed by Preston (55) and Darwish and Preston (56) in the rearrangement of trityl 2-methylbenzenesulfinate to the sulfone in acetonitrile.

Preston (55) and Darwish and Preston (56) have studied the rearrangement and substitution of a number of triphenylmethylarenesulfonates in a variety of non-hydroxylic solvents. The two compounds most extensively studied were triphenylmethyl 2-methylbenzenesulfinate and triphenylmethyl 2,6-dimethylbenzenesulfinate. In chloroform trityl 2-methylbenzene - sulfinate rearranges quantitatively to trityl 2-methylphenyl sulfone, with a half life for the first-order rearrangement of about twenty minutes at room temperature. Trityl 4-methylbenzenesulfinate rearranges at twice this rate, while trityl 2,6-dimethylbenzenesulfinate does not undergo rearrangement even under more vigorous reaction conditions. In fact all attempts to prepare trityl 2,6-dimethylphenyl sulfone were unsuccessful (55). Models

show this molecule to be highly hindered, and it is quite possible that the severe non-bonded interactions make the preparation of this molecule difficult.

When trityl 2-methylbenzenesulfinate was allowed to react with tetra-n-butylammonium azide in chloroform at room temperature, there was a concurrent substitution accompanying rearrangement resulting in the formation of trityl 2-methylphenyl sulfone, trityl azide and tetra-n-butylammonium 2-methylbenzenesulfinate as products of the reaction. An increase in the concentration of added azide ion resulted in an increase in the fraction of trityl azide produced, and a decrease in the fraction of trityl 2-methylphenyl sulfone formed. The formation of trityl azide was found to be an overall second-order process, first-order in ionic azide and first-order in sulfinate ester. Calculated first-order rate constants for the formation of trityl azide varied by a factor of 28 over a sixteen-fold concentration range of ionic azide, while calculated second-order rate constants varied by a factor of 2. The possibility that a direct displacement reaction was occurring on the ester by the azide ion was considered and rejected on the basis of the following observations.

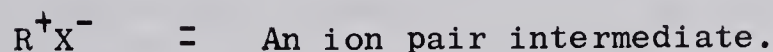
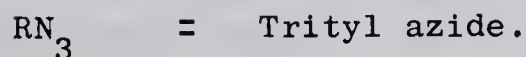
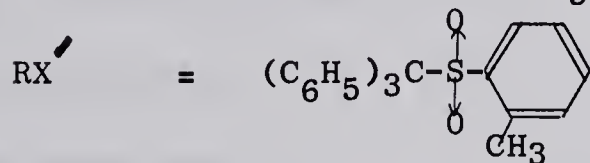
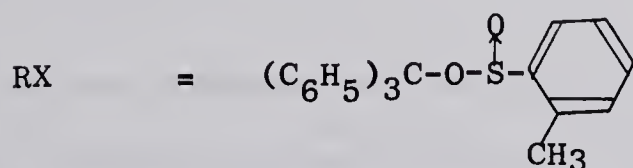
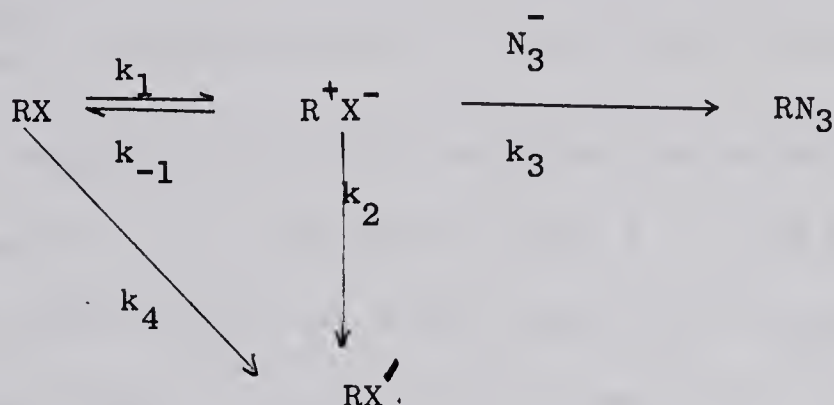
A comparison of the rates of exchange with equimolar concentrations of tetrabutylammonium azide and 2-methylbenzenesulfinate with trityl 2,6-dimethylbenzenesulfinate in chloroform showed that the pseudo-first-order rate constant ($k_{\text{ArSO}_2^-}$) for formation of trityl 2-methylphenyl sulfone is ca. $2.5 \times 10^{-6} \text{ sec.}^{-1}$, and the pseudo-first-order rate constant ($k_{\text{N}_3^-}$) for formation of trityl azide is $7.55 \times 10^{-6} \text{ sec.}^{-1}$ Preston (55) concluded that if a direct displacement reaction were operating here, these

values would not be expected to agree within a factor of three.

Preston (55) carried out competition experiments with trityl perchlorate, tetrabutylammonium azide and 2-methylbenzenesulfinate in chloroform, and if the results are used to calculate the azide/2-methylbenzenesulfinate competition factor a value of 2.11 ± 0.15 is obtained. The corresponding competition factor observed when trityl 2,6-dimethylbenzenesulfinate was allowed to react with azide ion and 2-methylbenzenesulfinate ion in chloroform is 3. The similar ratios observed, indicates that azide ion and 2-methylbenzenesulfinate ion are competing for the same type of species generated by trityl perchlorate or trityl 2,6-dimethylbenzenesulfinate in chloroform solvent. Since trityl perchlorate, is completely ionized it must be reacting as an ion pair or higher aggregate. It appears, that the substitution of trityl 2,6-dimethylbenzenesulfinate does not proceed via a direct displacement reaction under the present conditions. Analogously trityl 2-methylbenzenesulfinate would react in the same way during substitution since the only structural difference between this ester, and trityl 2,6-dimethylbenzenesulfinate is a methyl group in the six position of the benzene ring. Therefore the concurrent rearrangement and substitution of trityl 2-methylbenzenesulfinate with tetrabutylammonium azide, involve an ionic mechanism, and substitution is a result of exchange and not a direct displacement reaction.

The fact that a second-order nucleophilic displacement reaction is not taking place on the substrate, together with the observed reduced yields of sulfone on increasing the mole ratio of azide salt, strongly

suggests that both trityl azide and trityl 2-methylphenyl sulfone arise from a common ion pair intermediate. The following kinetic scheme suggested by Preston (55) best fits the results of the reaction of the 2-methyl ester with azide ion in chloroform.



Here k_4 represents the formation of sulfone by all other paths than through an intermediate which is capable of being trapped by nucleophiles. A complete kinetic analysis was made from this scheme and the following final expression was obtained,

$$\frac{1}{F_{\text{azide}}} = \frac{R(k_{-1} + k_2) + k_2}{k_3(\text{N}_3^-)} + (R + 1)$$

where $R = k_4/k_1$ and $F_{\text{azide}} = \frac{(RN_3)}{(RN_3) + (RX)}$ = fraction of RX

producing RN_3 .

A plot of $1/F_{\text{azide}}$ against $1/(N_3^-)$ will yield a straight line with slope $\frac{R(k_{-1} + k_2) + k_2}{k_3}$, and intercept $(R + 1)$. From the intercept a value of R can be obtained. When the nucleophile employed was azide ion such a plot (55) gave an intercept of 1, indicating that $R = 0$ and $k_4 = 0$. This showed that all the sulfone and trityl azide arose from a common intermediate, which in principle was capable of being trapped completely at sufficiently high azide concentration.

At room temperature the first-order rate constants for rearrangement of trityl 2-methylbenzenesulfinate to trityl 2-methylphenyl sulfone, in carbon tetrachloride is $3 \times 10^{-6} \text{ sec.}^{-1}$, in chloroform is $5 \times 10^{-4} \text{ sec.}^{-1}$, and in nitromethane is $1.3 \times 10^{-3} \text{ sec.}^{-1}$, (55, 56). The increase in the first-order rate constants as the ionizing power of the solvent is increased suggests that an ionic reaction is taking place.

In acetonitrile solutions, when tetra-n-butylammonium azide was employed as the nucleophile; a portion of the product sulfone was diverted to trityl azide, but the rate of disappearance of the ester was not affected. At a constant concentration of ester and at a 0.010 M concentration of ionic azide the first-order rate constant for the disappearance of ester is $1.1 \pm 0.1 \times 10^{-3} \text{ sec.}^{-1}$. The amount of trityl azide produced is 33%. When the concentration of azide ion was increased to 0.230 M, the rate of

disappearance of ester is $1.0 \times 10^{-3} \text{ sec.}^{-1}$, and the amount of trityl azide produced is 45% (55, 56).

A competition reaction was carried out by adding trityl perchlorate to an acetonitrile solution of equimolar concentrations of tetrabutylammonium azide and 2-methylbenzenesulfinat. The trityl perchlorate reacted essentially instantaneously with the salts. Three minutes after the reactants were mixed about 45% trityl azide was formed, and increased to about 55% after one hour. The amount of trityl 2-methylphenyl sulfone also increased with time. These observations are consistent with the formation of trityl azide, trityl 2-methylphenyl sulfone and trityl 2-methylbenzenesulfinat as initial products of the reaction.

The exchange reactions involving the azide salt, together with the competition reactions, suggest that the majority of sulfone produced on rearrangement of trityl 2-methylbenzenesulfinat to the corresponding sulfone in the presence of large excesses of azide salt, arise through an intermediate that cannot be easily trapped by azide ion. Thus two distinct ionic species were proposed, an intimate ion pair, which was not easily diverted to trityl azide, and a solvent separated ion pair or free ions , or both which could be equated with the trappable species (55, 56).

It seemed desirable to make further studies on the reaction of trityl 2-methylbenzenesulfinat in both solvents chloroform and acetonitrile. In the former solvent it was desired to try to gain further information which could show whether or not an ionic intermediate was precursor of the

exchange products. In acetonitrile it was desired to attempt the characterization of the capturable and non-capturable species.

CHAPTER I

The Reaction of Trityl 2-methylbenzenesulfinate with some Tetra-n-butyl- ammonium salts in chloroform at 25°C.

INTRODUCTION

In this chapter the preparation of triphenylmethyl 2-methylbenzenesulfinate and some related compounds are described. Exchange reactions with tetra-n-butylammonium benzoate and p-nitrobenzoate salts in chloroform at 25° together with product isolation are also presented. The reaction of benzyl 2-methylbenzenesulfinate with tetra-n-butylammonium azide in chloroform is also included.

RESULTS

2-Methylbenzenesulfinic acid was prepared by treatment of o-toluidine with nitrous acid (58). The solution was saturated with sulfur dioxide followed by addition of copper powder, to yield the acid.

Treatment of 2-methylbenzenesulfinic acid with thionyl chloride in pentane gave rise to the acid chloride. Triphenylcarbinol dissolved in pyridine was then allowed to react with the acid chloride at methanol-ice temperatures. The ester was then isolated and recrystallized from ether-pentane or ether.

There are several precautions which must be adhered to if the ester is to be isolated in a pure form. The complete utilization of the triphenylcarbinol must be ensured, by employing a two fold excess of acid chloride.

The crucial step in the preparation is the work-up procedure, which consists of pouring the reaction mixture into ice containing hydrochloric acid, followed by extraction with ether. If the pyridine was completely removed by neutralization with hydrochloric acid, then hydrolysis of the ester readily occurred on washing the ethereal extracts with water (55). It is also possible that some rearrangement of ester to trityl 2-methylphenyl sulfone may occur. Initial samples of the ester prepared by Preston (55) contained the sulfone as an impurity. Also initial samples of the ester prepared during the present study contained from ca. 7 to 25% sulfone.

There are two methods whereby trityl 2-methylbenzenesulfinate may be obtained free of any trityl 2-methylphenyl sulfone. The first method involved a low temperature work-up, which presumed that any sulfone formed during the preparation of the ester was formed as a result of temperature changes during isolation. All solutions used in the work-up (ether, water etc.) were cooled to about 0 - 5° before use. At no time during the work-up was the ether solution of the ester allowed to warm up to room temperature. Recrystallization involved using an excess of cold ether to dissolve the crude ester. Most of the ether was removed at the aspirator and the resulting solution cooled. Ester collected after filtration has been found to be free of sulfone. A second crop of pure ester may be collected by evaporation of 50% of the mother liquor, followed by further cooling and filtration.

The second method utilized for obtaining trityl 2-methylbenzenesulfinate free of trityl 2-methylphenyl sulfone, involved fractional crystallization from 50% ether-pentane. The first batch of crystals isolated

by a method of evaporative crystallization from this solvent mixture is rich in sulfone impurity. The second crop of crystals obtained from the mother liquor has been found to be free of sulfone. The infrared and n.m.r. spectra are consistent with trityl 2-methylbenzenesulfinate .

Benzyl 2-methylbenzenesulfinate was prepared by the same method used to make benzyl 2,6-dimethylbenzenesulfinate (61). Treatment of 2-methylbenzenesulfinic acid with thionyl chloride gave rise to 2-methylbenzenesulfinyl chloride. Benzyl alcohol in pyridine was then allowed to react with acid chloride at Dry Ice-acetone temperatures. The ester was then isolated and recrystallized from ether-pentane. The infrared spectrum (carbon disulfide) showed strong bands at 700, 760, 910, and 1140 cm^{-1} . Bellamy (59) has described the region around 1140 cm^{-1} , as being characteristic of sulfinate ester absorption.. The n.m.r. spectrum (carbon disulfide) showed signals at 2.15 (q), 2.6 -3.0 (m), 5.32 (d) 5.55 (d) and τ 7.68 (s). The quartet at low field, equivalent to one proton is due to the hydrogen ortho to the sulfur in the arenesulfinate group. The multiplet at low field, equivalent to eight hydrogens is due to the remaining eight aromatic protons. The two doublets at, τ 5.32 and τ 5.55 equivalent to two hydrogens are due to the methylene hydrogens ($J = 11.5$ cps.). The singlet at high field, τ 7.68, is due to the three methyl protons attached to the aromatic ring. The ratio of the integrated intensities of the aromatic protons to methyl protons is 4.6 : 1.5 : 1. calculated 4.5 : 1.5 : 1.

Preparation of reaction products.

Benzyl azide was prepared by the method described by Curtius and

Ehrhart (74) by treating benzyl chloride with sodium azide in refluxing absolute ethanol.

Trityl 2-methylphenyl sulfone may be conveniently synthesized by the method described by Preston (55), which consisted of refluxing trityl 2-methylbenzenesulfinate in chloroform. However during the course of the present study, an attempted synthesis of trityl 2-methylbenzenesulfinate resulted in the isolation of trityl 2-methylphenyl sulfone as the only product. The crude sulfone obtained after work-up was recrystallized from warm ether-chloroform.

Trityl benzoate was prepared according to the procedure outlined by von E. Doering et al (60). Benzoyl chloride and the potassium salt of triphenylcarbinol were allowed to react in xylene to yield trityl benzoate after work-up.

Treatment of trityl perchlorate with sodium p-nitrobenzoate in acetonitrile gave rise to trityl p-nitrobenzoate. The product after work-up was recrystallized from a minimum amount of purified acetonitrile. The infrared spectrum (chloroform) showed strong bands at 1110, 1275, 1356, 1530, 1612, and 1732 cm^{-1} .

Product isolation procedure.

Treatment of trityl 2-methylbenzenesulfinate with tetra-n-butylammonium benzoate in chloroform yielded trityl benzoate and trityl 2-methylphenyl sulfone. Similarly treatment of the 2-methyl ester with tetra-n-butylammonium p-nitrobenzoate gave rise to trityl p-nitrobenzoate

and trityl 2-methylphenyl sulfone.

In studying the kinetics of the rearrangement of trityl 2-methylbenzenesulfinate to trityl 2-methylphenyl sulfone in chloroform with added 2,6-lutidine or azide ion, it was possible to follow the appearance of the sulfone absorption at 1310 cm^{-1} . However in the presence of tetra-n-butylammonium benzoate and p-nitrobenzoate the appearance of the sulfone absorption could not be followed due to interference in this region by bands from these salts, and therefore kinetic measurements were not made. It was however possible to study the products of the reaction of the ester with benzoate and p-nitrobenzoate salts in chloroform and to determine the amounts of trityl benzoate and trityl p-nitrobenzoate produced by quantitative infrared measurements.

In the absence of kinetic data for the reaction of trityl 2-methylbenzenesulfinate with tetrabutylammonium benzoate and p-nitrobenzoate in chloroform, 4 hours were estimated as the time needed for the reaction to reach completion. This estimate was made in the following way. The half-life for the reaction of trityl 2-methylbenzenesulfinate in chloroform in the absence of salt is 22 minutes. The rate of reaction in the presence of quaternary ammonium salts should be approximately equal to or faster than in the absence of these salts. Therefore 4 hours (10 half-lives) is a good estimate as the time required for the reaction of trityl 2-methylbenzenesulfinate with tetrabutylammonium benzoate or p-nitrobenzoate to reach completion. Therefore mixtures of the reactants in chloroform were allowed to stand at $25.00 \pm 0.01^{\circ}$ for 4 hours. After this time the mixtures

were worked up and the products isolated.

After isolation of the products, the absorbance of the benzoate esters were determined, and from the appropriate Lambert-Beer plot the concentrations were calculated. By dividing the concentration of benzoate ester by the concentration of starting trityl 2-methylbenzenesulfinate the fraction or percentage trityl benzoate or trityl p-nitrobenzoate was determined.

Control Experiments

Synthetic mixtures consisting of trityl benzoate, tetra-n-butyl-ammonium benzoate and 2,6-lutidine were dissolved in 50 ml. chloroform and transferred to a separatory funnel. The mixture was then carried through the same extraction procedure used in the product runs. Total spectra, both infrared and nuclear magnetic resonance showed that a minimum of nine washings with 100 ml of water were necessary to remove all traces of benzoate salts. In Table I the results of such control experiments are presented.

TABLE I

CONTROL ISOLATION OF TRITYL BENZOATE FROM CHLOROFORM.

Run	Trityl benzoate Grams.		Concentration Molar		%Recovery
	<u>Weighed</u>	<u>Found</u>	<u>Calc.</u>	<u>Found</u> ^(a)	
3-38	0.4212	0.4876	0.02420	0.0230	95%
3-45	.2106	.2003	.01210	.0109	90%
3-42	.0505	.0812	.00290	.0026	90%
3-44	.0512	.0504	.00294	.0026	88.5%

(a) - Determined from the plot of absorbance v.s. concentration.

The results of Table I, indicate that from 88 - 95% of the trityl benzoate can be isolated by the procedure used. Run 3-38 and 3-42 show a high weight recovery. In run 3-38, 4 washings with 75 ml. of water was used. Infrared and n.m.r. spectra indicated the presence of some residual salt which probably accounted for the high weight observed. In run 3-42, 6 water washings were employed. Runs 3-44 and 3-45, needed 9 washings with 100 ml. of water, the minimum amount necessary for removal of all traces of salt.

Synthetic mixtures of trityl p-nitrobenzoate, tetra-n-butyl-ammonium p-nitrobenzoate and 2,6-lutidine were also subjected to the same extraction procedure. These results are given in Table II.

TABLE II

CONTROL ISOLATION OF TRITYL p-NITROBENZOATE FROM CHLOROFORM.

Run	Trityl <u>p</u> -nitrobenzoate Grams.		Concentration ₃ Molar x 10 ³		%Recovery
	Weighed	Found	Calc.	Found ^(a)	
3-50	0.1036	0.0835	5.064	4.03	79.6%
3-54	.0912	.0754	4.455	3.60	80.6%
3-52	.0714	.0571	3.487	2.75	79.0%
3-56	.0306	.0261	1.497	1.23	82.1%

(a) - Determined from the plot of absorbance v.s. concentration.

These control experiments served to establish the recovery percentage of the benzoate esters, and to indicate the extent of the stability

of these esters under the work-up conditions.

In order to determine the percent trityl benzoate or trityl p-nitrobenzoate produced in a particular run by infrared measurements, it was necessary to determine the relationship between optical density and concentration for both of these esters in chloroform.

Standard solutions of trityl benzoate were prepared in chloroform and the optical density determined at 1718 cm.^{-1} . The relationship between optical density and concentration for trityl benzoate in chloroform is given in Table III, and Figure II.

TABLE III

RELATIONSHIP BETWEEN OPTICAL DENSITY AND CONCENTRATION FOR TRITYL BENZOATE AS MEASURED IN CHLOROFORM AT 1718 cm.^{-1}

Ester x 10^2 Molar	I_0/I	Log $(I_0/I) \times 10$
2.912	4.265	6.300
2.329	3.212	5.067
1.747	2.482	3.949
1.165	1.906	2.802
0.582	1.385	1.426
0.291	1.176	0.7096

Table IV and Figure III, present the relationship between optical density and concentration for trityl p-nitrobenzoate in chloroform by the

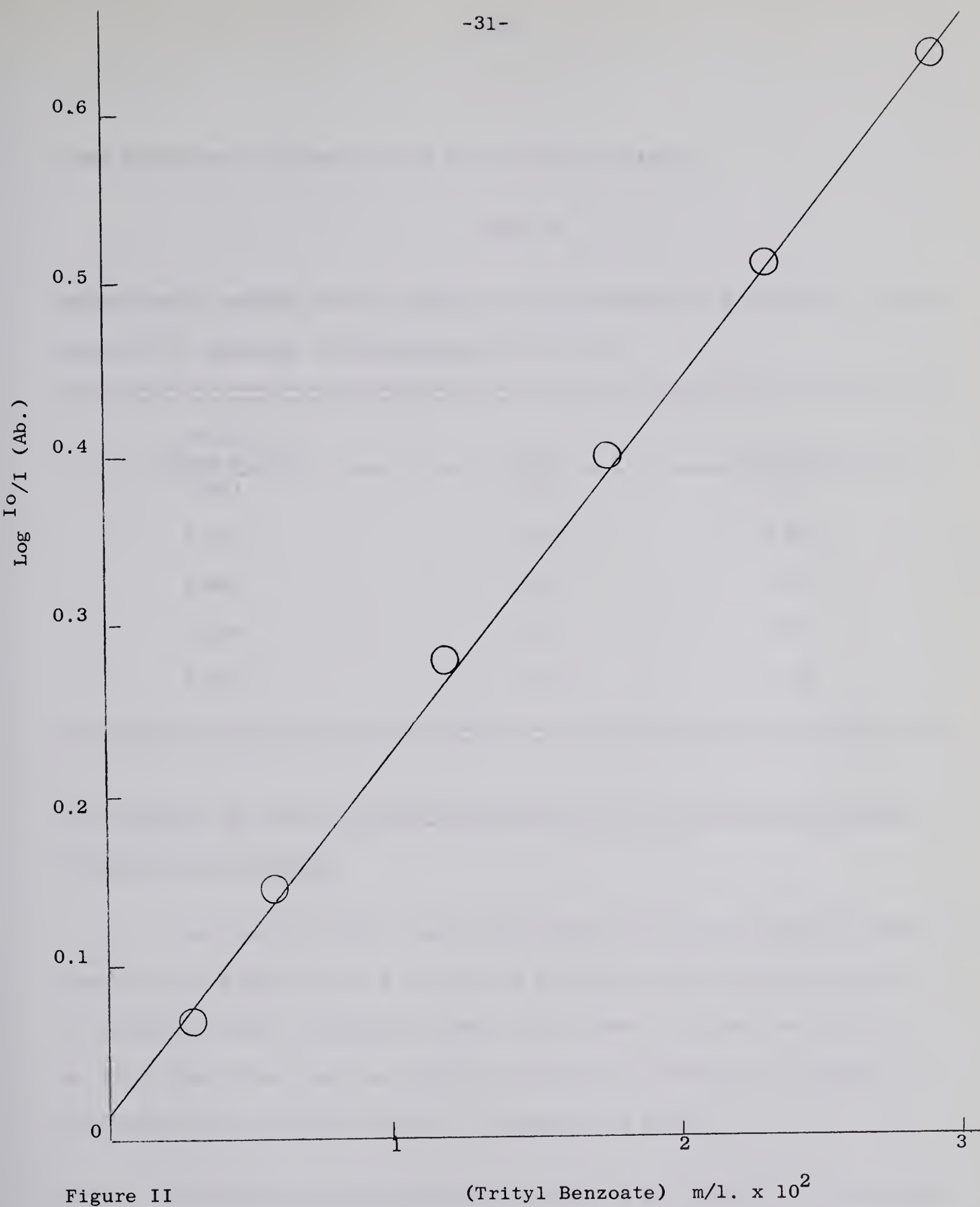


Figure II

Relationship between optical density and concentration for Trityl benzoate in chloroform at 1718 cm.^{-1}

same procedure outlined for the trityl benzoate ester.

TABLE IV

RELATIONSHIP BETWEEN OPTICAL DENSITY AND CONCENTRATION FOR TRITYL p-NITRO-BENZOATE AS MEASURED IN CHLOROFORM AT 1732 cm^{-1}

Benzoate Molar $\times 10^2$	I_0/I	$\text{Log } (I_0/I) \times 10$
1.391	2.275	3.571
1.113	1.935	2.868
0.835	1.651	2.178
0.556	1.411	1.493
0.278	1.182	0.728

The reaction of trityl 2-methylbenzenesulfinate with tetrabutylammonium benzoate in chloroform.

A mixture of trityl 2-methylbenzenesulfinate and tetrabutylammonium benzoate was dissolved in a chloroform solution containing 2,6-lutidine in a volumetric flask, thoroughly shaken and allowed to stand for four hours at 25° . After this time the reaction mixture was worked up. A summary of the results of a series of runs is presented in Table V.

The percent trityl benzoate as reported in Table V, is a corrected value. A correction was made based on the presence of 7% trityl 2-methylphenyl sulfone in the starting ester. A further correction was made based

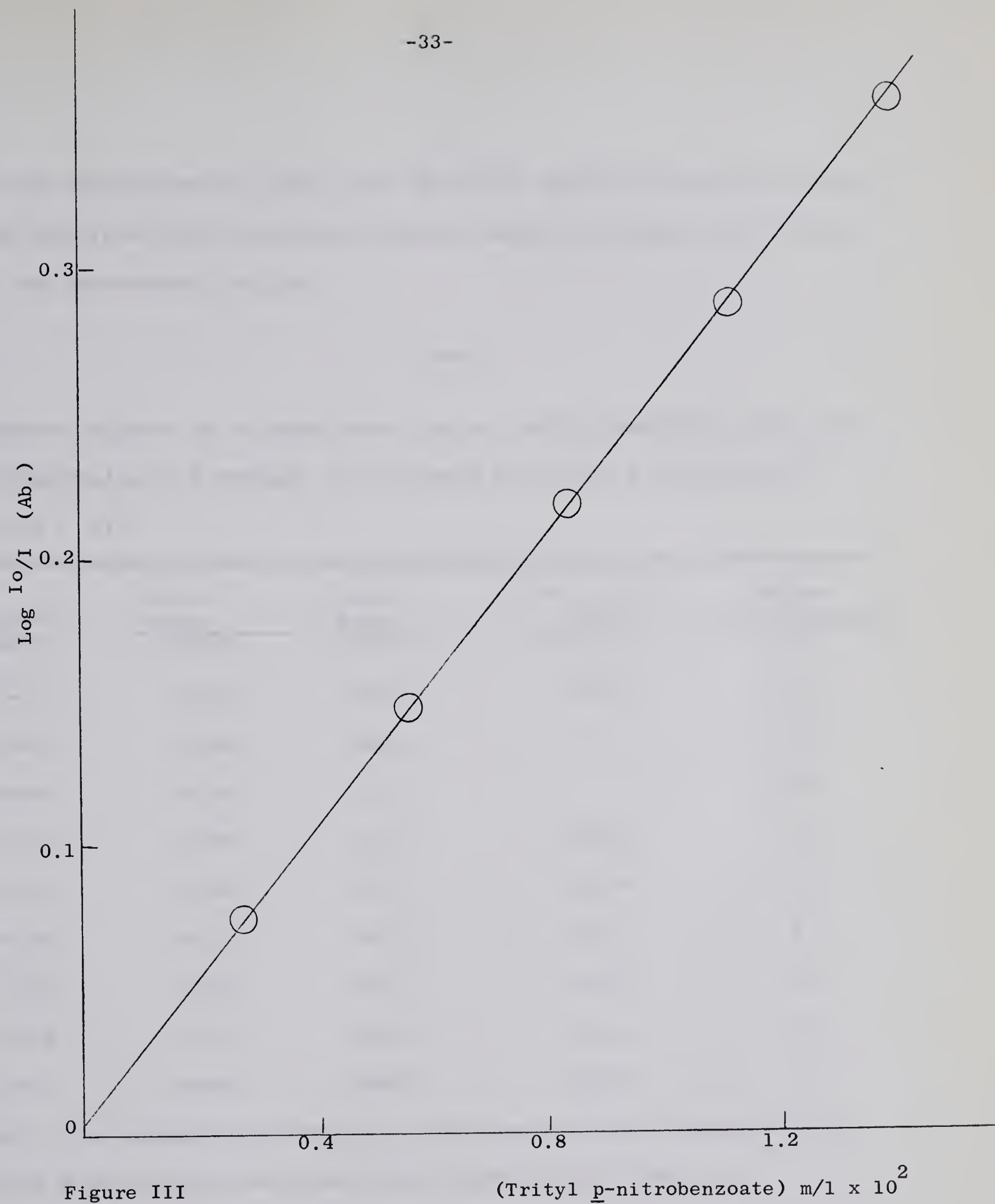


Figure III

Relationship between optical density and concentration for
Trityl p-nitrobenzoate in Chloroform at 1732 cm^{-1}

on the calibration run, where only 90% trityl benzoate could be recovered. The details of these corrections and the isolation procedure are outlined in the experimental section.

TABLE V

PRODUCT ANALYSIS OF THE REACTION OF TRITYL 2-METHYLBENZENESULFINATE WITH TETRABUTYLAMMONIUM BENZOATE IN CHLOROFORM CONTAINING 2,6-LUTIDINE AT $25.00 \pm .01^{\circ}$.

Run (a)	(Ester) Molar	(Salt) Molar	(2,6-lutidine) Molar	Percent Trityl Benzoate
4-62	0.02347	0.44262	0.03022	41.1
3-56	.02178	.19324	.03559	35.1
3-46	.02145	.18252	"	32.2
3-58	.02259	.12122	"	26.4
3-120	.02089	.05359	.03564	9.6
3-104	.02197	.05142	.03559	8.1
3-122	.02153	.02679	.03564	4.3
3-106	.02242	.02571	.03559	4.6
3-118	.02073	.02333	.03564	3.5
3-64	.02049	.02227	.03559	2.7

(a) - The run number as used is a laboratory note book reference, e.g.

3-56 refers to page 56 of the third laboratory note book.

It was possible to reproduce results within reasonable experimental

error, (run 3-64 compared to run 3-118). The results seem to be consistent with the fact that at higher tetra-n-butylammonium benzoate concentrations a greater amount of trityl benzoate is produced. It should be noted that these results are subject to fairly large experimental errors, as was indicated by the control experiments.

The reaction of trityl 2-methylbenzenesulfinate with tetra-n-butylammonium p-nitrobenzoate in chloroform.

Treatment of trityl 2-methylbenzenesulfinate with tetra-n-butylammonium p-nitrobenzoate in chloroform containing 2,6-lutidine yielded trityl p-nitrobenzoate as one of the products of the reaction. Table VI presents the results obtained when the concentration of tetra-n-butylammonium p-nitrobenzoate was varied while that of the trityl 2-methylbenzenesulfinate ester was kept relatively constant. At a salt concentration of 0.20 M, 29% trityl p-nitrobenzoate was formed. At lower concentrations of p-nitrobenzoate salt smaller amounts of ester were isolated. Runs 3-110 and 3-124 were intended as duplicates, and the results show good agreement.

The percentage trityl p-nitrobenzoate listed in Table VI is a corrected value. Corrections were made based on the control experiments where 80% trityl p-nitrobenzoate could be recovered. A further correction was made based on the presence of 7% trityl 2-methylphenyl sulfone in the starting trityl 2-methylbenzenesulfinate.

TABLE VI

PRODUCT ANALYSIS OF THE REACTION OF TRITYL 2-METHYLBENZENESULFINATE
WITH TETRABUTYLAMMONIUM p-NITROBENZOATE IN CHLOROFORM CONTAINING
2,6-LUTIDINE AT $25.00 \pm .01^{\circ}$.

Run	Ester Molar	Salt Molar	2,6-lutidine Molar	%Trityl <u>p</u> -nitro- benzoate
3-108	0.02300	0.20156	0.03551	29.4
3-124	.02138	.10263	.03101	18.6
3-110	.02179	.10078	.03551	19.8
3-112	.02200	.05039	.03551	13.0
3-116	.02460	.04163	.03559	11.7

The reaction of Benzyl 2-methylbenzenesulfinate with tetrabutylammonium
azide in chloroform.

The expected mode of reaction of benzyl 2-methylbenzenesulfinate with azide ion in chloroform, is attack of azide on the primary carbon displacing the arenesulfinate group and giving rise to benzyl azide as one of the reaction products. The rate of reaction of benzyl 2-methylbenzenesulfinate with tetrabutylammonium azide was studied by following the change in optical density at 2104 cm^{-1} , with time.

A plot of optical density against concentration for benzyl azide in chloroform is not linear. Such a plot is presented in Figure IV. The numbers from which this plot was obtained is presented in Table VII. The procedure used for the Lambert-Beer law determination was

identical to that described previously.

TABLE VII

RELATIONSHIP BETWEEN OPTICAL DENSITY AND CONCENTRATION FOR BENZYL AZIDE
IN CHLOROFORM AT 2104 cm^{-1}

Benzyl Azide mg/ml	I_0/I	Log I_0/I
5.56	9.500	0.9777
4.45	6.786	.8316
3.38	4.507	.6539
2.23	2.761	.4411
1.12	1.688	.2274

In Table VIII the results of a run involving benzyl 2-methylbenzenesulfinate and tetrabutylammonium azide in chloroform are given. From the absorbance values the concentration in mg./ml., of benzyl azide was obtained from the plot of absorbance against concentrations (Figure VII). The rate constants were calculated from the formula $kt = 2.303 \log \left(\frac{C_\infty - C_0}{C_\infty - C} \right)$, where C is the concentration of benzyl azide produced at anytime t, C_0 is the concentration of benzyl azide at time t zero, and C_∞ is the concentration of benzyl azide produced at the end of the reaction. Due to the slow nature of this reaction ($t_{1/2} \approx 80$ days), the theoretical infinity was used to calculate the rate constants, and is equivalent to 5.08 mg./ml. , of benzyl azide.

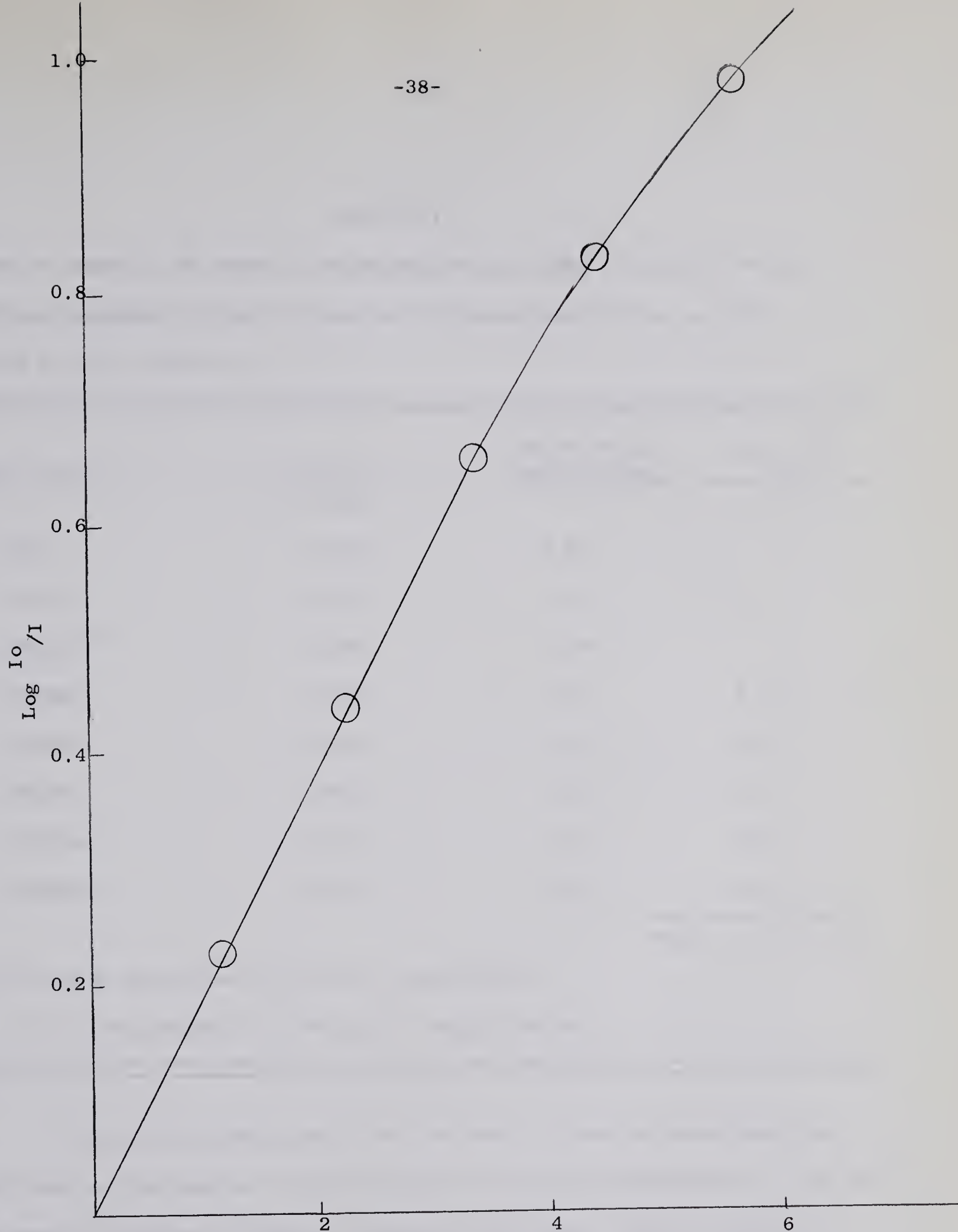


Figure IV

mg/ml (Benzyl azide)

Relationship between optical density and concentration
for Benzyl azide in chloroform at 2104 cm.⁻¹

TABLE VIII

RATE OF REACTION OF BENZYL 2-METHYLBENZENESULFINATE (0.03815 M) WITH
TETRABUTYLAMMONIUM AZIDE (0.06231 M) IN CHLOROFORM AT 2104 cm.⁻¹ AT
25.00 ± .01° . RUN 4-64

Time (sec.)	Log I ₀ /I	Concentration mg/ml (Cobs.)	k ₁ x 10 ⁷ sec. ⁻¹
0	0.01223	-	-
6810	.01379	0.05	-
61595	.01727	.055	-
85625 ^(a)	.01803	.058	-
335385	.05834	.28	1.79
434290	.06454	.33	1.58
691425	.07878	.39	1.17
1030125	.1045	.53	1.04
2465890	.2653	1.35	1.15
Avg =			1.33 ± .27

(a) Taken as zero time in the rate calculation.

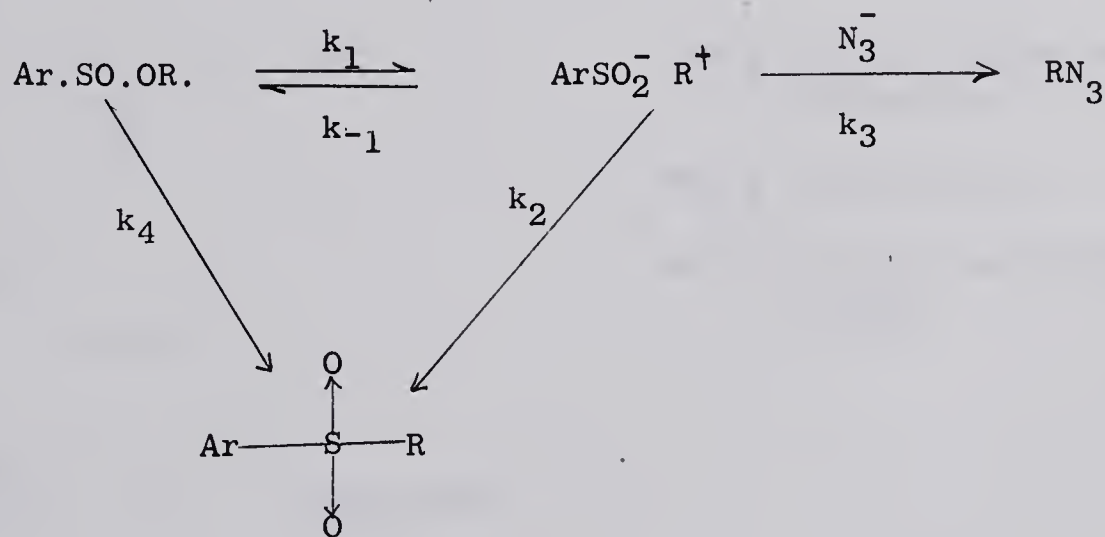
C_∞ is equivalent to 5.08 mg./ml. benzyl azide.

After each kinetic point was recorded a total infrared spectrum was taken of the sample. From the total spectrum the absorbance at 1125 cm.⁻¹ was seen to gradually reduce in intensity with time. From the spectrum taken after 2.47 x 10⁶ secs. the peak at 1125 cm.⁻¹, showed that benzyl 2-methylbenzenesulfinates was still present in the reaction mixture, indicating that under these conditions sulfur-oxygen bond fission is not an important reaction.

DISCUSSION

Preston (55) has demonstrated that a common intermediate gave rise to the substitution and rearrangement products of the reaction of trityl 2-methylbenzenesulfinate with tetrabutylammonium azide in chloroform. This intermediate may be an ion pair or the substrate itself. Preference was given to the mechanism involving the ion pair, but this is not the only mechanism with which the results are consistent. Consider the two possible mechanisms:

Mechanism I



Ar = 2-methylphenyl

R = Trityl

From a kinetic treatment Preston derived the following expression,

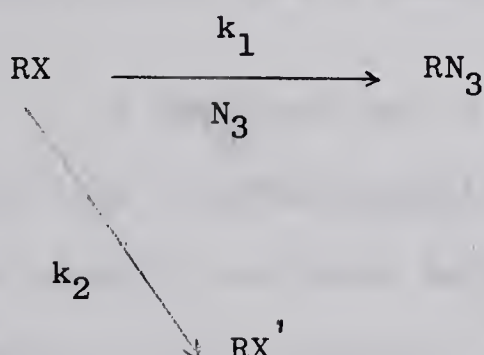
$$\frac{1}{\text{F azide}} = \frac{R(k_{-1} + k_2) + k_2}{k_3(\text{N}_3^-)} + (R + 1), \text{ where } R = k_4/k_1.$$

From a plot $1/F_{\text{azide}}$ against $1/(N_3^-)$ a straight line should be obtained with slope, $\frac{R(k_{-1} + k_2) + k_2}{k_3}$, and intercept $(R + 1)$. Such

a plot (55) yielded a straight line with an intercept of 1. Therefore $R = 0$, and $k_4 = 0$. When these values are substituted in the original equation, $1/F_{\text{azide}} = \frac{k_2}{k_3(N_3^-)} + 1$.

In the same manner a reaction scheme may be set up in which an intermediate is excluded.

Mechanism II



$\text{RX} =$ Trityl 2-methylbenzene-sulfinate

$\text{RN}_3 =$ Trityl azide

$\text{RX}' =$ Trityl 2-methylphenyl-sulfone

$$\frac{d(\text{RN}_3)}{dt} = k_1(N_3)(\text{RX})$$

$$\frac{d(\text{RX}')}{dt} = k_2(\text{RX})$$

$$\frac{(\text{RX}')}{(\text{RN}_3)} = \frac{k_2}{k_1(N_3)}$$

$$\text{Let } F_{\text{azide}} = \frac{(\text{RN}_3)}{(\text{RN}_3) + (\text{RX}')} = \text{Fraction of RX producing RN}_3$$

$$\begin{aligned} \text{then } \frac{1}{F_{\text{azide}}} &= \frac{(RX') + 1}{(RN_3)} \\ &= \frac{k_2}{k_1(N_3)} + 1 \end{aligned}$$

A plot of $\frac{1}{F_{\text{azide}}}$ against $\frac{1}{(N_3)}$ will yield a straight line with slope $= k_2/k_1$ and intercept $= 1$.

Both schemes give rise to an equation of the same form indicating that both reaction pathways are consistent with the results (55). The characteristic common to both schemes is that sulfone and azide must arise directly from a common species.

It was hoped that a study of relative nucleophilicities, employing salts like tetrabutylammonium benzoate and p-nitrobenzoate might give some insight into which mechanism was operating under these conditions. However it is not possible to study the kinetics of the reaction of trityl 2-methylbenzenesulfinate with tetrabutylammonium benzoate and p-nitrobenzoate in chloroform. It was however possible to study the products of the reactions and thereby it was hoped to obtain relative second-order rate constants in a manner analogous to the treatment afforded the results of the reaction of the ester with tetrabutylammonium azide.

Reactions of trityl 2-methylbenzenesulfinate with tetrabutylammonium benzoate.

A plot of the inverse fraction of trityl benzoate produced against the inverse concentration of tetra-n-butylammonium benzoate is presented

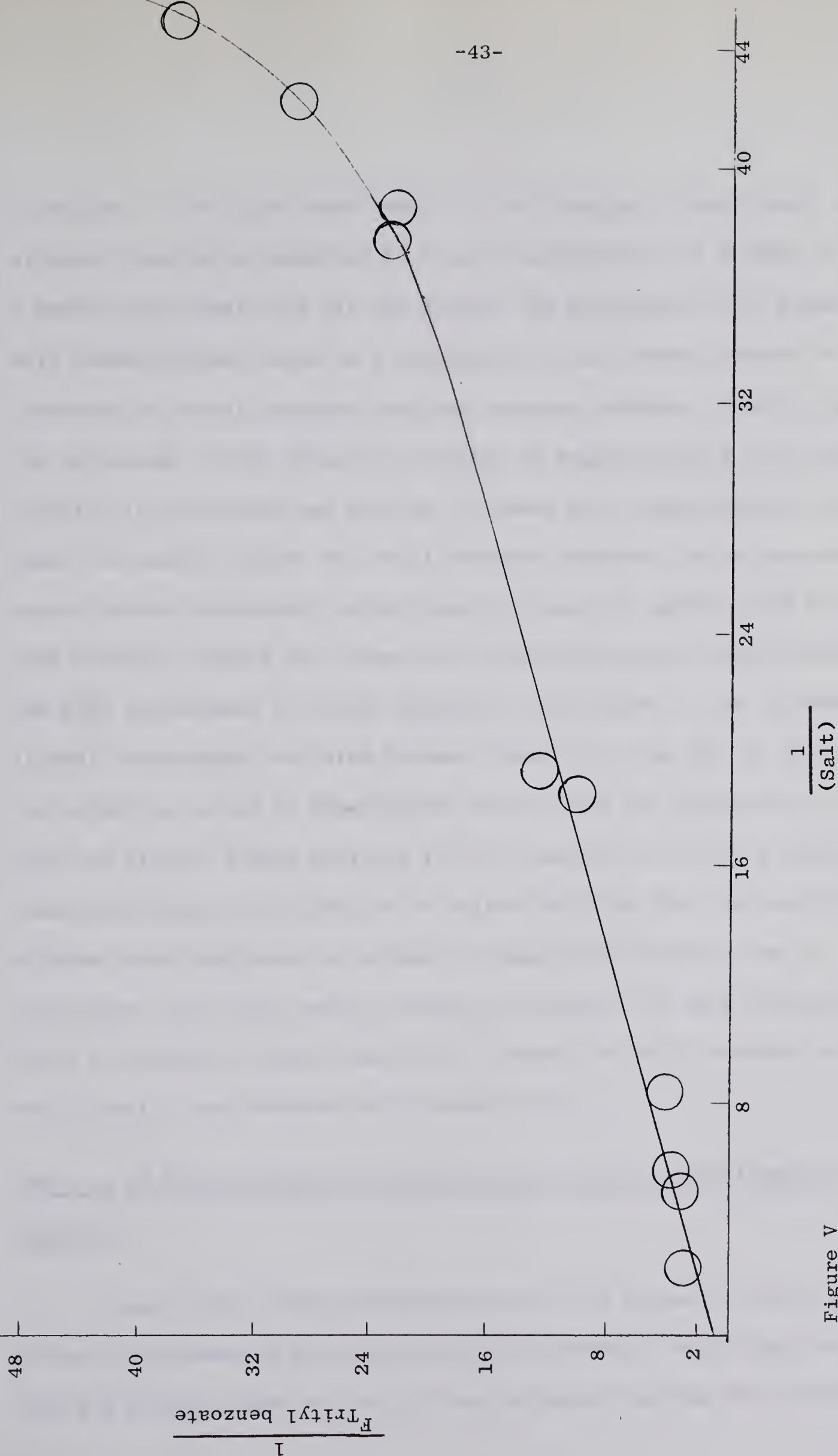


Figure V

Relationship between the inverse fraction of Trityl benzoate produced and the inverse concentration of tetrabutylammonium salt in chloroform at 25°C.

in Figure V . The plot shows that this relationship is not linear. A straight line may be drawn up to a salt concentration of 0.02571 M., but a smooth curve best fits all the points. The curvature of this graph at low salt concentrations could be a reflection of the errors involved in the isolation of trityl benzoate from the reaction mixture. A small error in the percentage trityl benzoate recovered is magnified when the inverse fraction is calculated and plotted. At lower salt concentrations which result in smaller amount of trityl benzoate produced, the experimental errors become increasingly significant. It must be assumed that the most reliable results are those which involve high salt concentrations and high percentages of trityl benzoate. From Figure V, the intercept is best approximated as lying between 0 and 2. If the plot is linear and the curvature is due to experimental errors, and the intercept is 1, then the kinetic scheme outlined for the reaction of trityl 2-methylbenzenesulfinate with azide ion in chloroform also fits the results obtained when this ester is allowed to react with benzoate ion in chloroform. Then there would be a common capturable ion pair intermediate, which is capable of being completely diverted to trityl benzoate at a sufficiently high benzoate salt concentration.

Reaction of Trityl 2-methylbenzenesulfinate with tetrabutylammonium p-nitrobenzoate.

When trityl 2-methylbenzenesulfinate was allowed to react with tetra-n-butylammonium p-nitrobenzoate in chloroform containing 2,6-lutidine, trityl p-nitrobenzoate and trityl 2-methylphenyl sulfone were produced in

amounts dependent on the concentration of p-nitrobenzoate salt used. The percentage of trityl p-nitrobenzoate formed increased as the concentration of salt was increased and the percentage of trityl 2-methylphenyl sulfone decreased, (Table VI).

The relationship between the inverse fraction of trityl p-nitrobenzoate produced and the inverse concentration of tetra-n-butylammonium p-nitrobenzoate is presented in Figure VI. The intercept is 1.8 .

The results obtained from the reaction of trityl 2-methylbenzenesulfinate with tetrabutylammonium p-nitrobenzoate in chloroform is not applicable to a treatment afforded the results of the reaction of the ester with tetrabutylammonium azide in chloroform, since a plot of the relationship between 1/Fraction of trityl p-nitrobenzoate and 1/concentration of tetrabutylammonium p-nitrobenzoate, did not yield an intercept of 1. Although it is possible that this discrepancy may be due to experimental error, no conclusions can be drawn from these results.

The Correlation between Structure and Reactivity.

When trityl 2-methylbenzenesulfinate was allowed to react with tetrabutylammonium azide (0.046 M) in chloroform the rate constant observed for disappearance of ester is $9.14 \pm 0.33 \times 10^{-4} \text{ sec.}^{-1}$ Under analogous conditions but with a tetrabutylammonium azide concentration of 0.062 M, benzyl 2-methylbenzenesulfinate yielded a rate constant equal to $1.34 \pm 0.28 \times 10^{-7} \text{ sec.}^{-1}$ If an S_N2 type of reaction were occurring on both systems then one would expect the reaction of benzyl 2-methylbenzene-

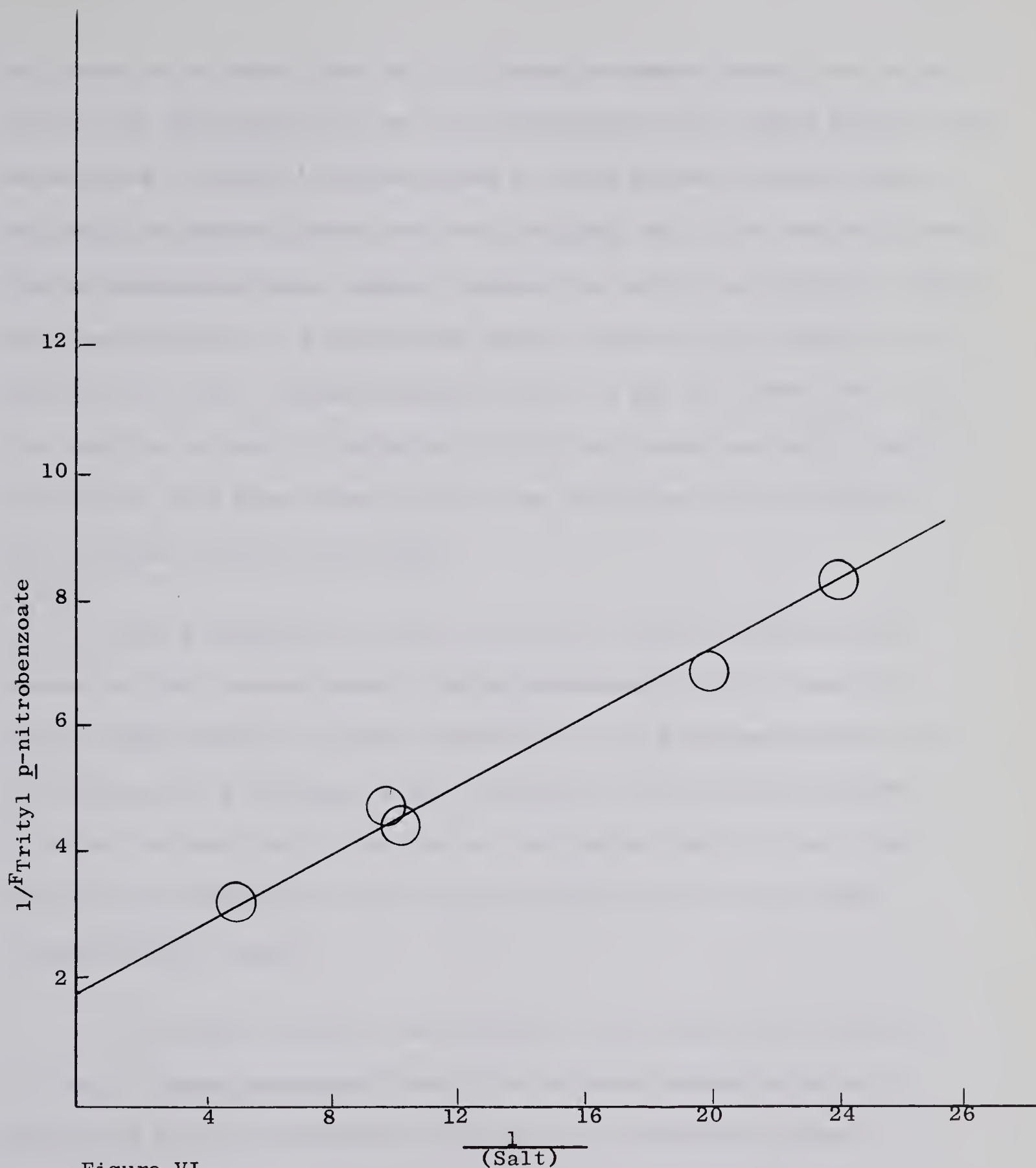


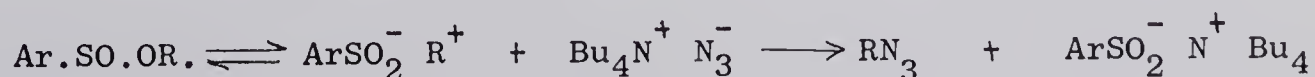
Figure VI

Relationship between the inverse fraction of Trityl p-nitrobenzoate produced and the inverse concentration of tetrabutylammonium p-nitrobenzoate added in chloroform at 25°C.

sulfinate to be faster than trityl 2-methylbenzenesulfinate. Due to the steric bulk associated with the trityl group the three phenyl groups would be expected to hinder backside attack by azide on the tertiary carbon. Replacing two phenyl groups with two hydrogens, as is the case with benzyl 2-methylbenzenesulfinate, should increase the rate of nucleophilic bimolecular substitution by a substantial margin. However it is seen that the reaction of trityl 2-methylbenzenesulfinate is ca. 10^4 times faster than the reaction of benzyl 2-methylbenzenesulfinate under analogous reaction conditions. From these considerations the reactions must be occurring by two different reaction mechanisms.

From a comparison of the structures of the two arenesulfinate esters one would expect benzyl 2-methylbenzenesulfinate to react by a pathway that involves a direct displacement of the arenesulfinate group by azide ion in a concerted manner. Therefore trityl 2-methylbenzenesulfinate is most likely reacting by a mechanism that involves a rate determining ionization, since this ester generates the very stable triphenylmethyl cation.

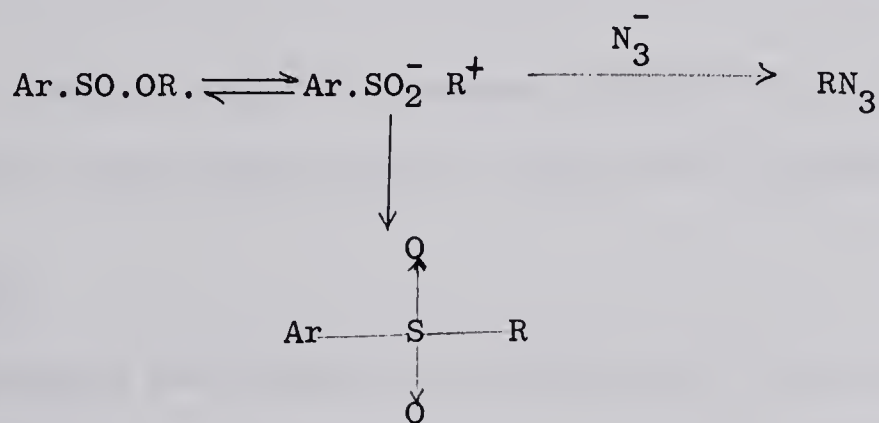
It is thus felt that the results of the substitution reaction of trityl 2-methylbenzenesulfinate with tetrabutylammonium azide in chloroform are best explained by an ion pair exchange mechanism as in the following scheme.



By analogy the reactions of trityl 2-methylbenzenesulfinate, with

tetrabutylammonium benzoate and p-nitrobenzoate to yield trityl benzoate and trityl p-nitrobenzoate respectively in chloroform solvent must be proceeding by a mechanism as depicted above. Whether the intermediate is an intimate or solvent speparated ion pair or both cannot be deduced from the present results. However the presence of dissociated ions is precluded since the reaction was carried out in chloroform (13, 23).

If the substitution reaction is proceeding by way of an ion pair intermediate, then the rearrangement of trityl 2-methylbenzenesulfinate in chloroform to trityl 2-methylphenyl sulfone must be occuring via this same intermediate. Therefore the mechanism as outlined below and first suggested by Preston (55) is consistent with the observed facts.



EXPERIMENTAL

Physical Measurements

Melting points were taken on a Hershberg melting point apparatus using a set of Anschutz thermometers. The melting points reported are uncorrected.

Refractive indices were measured on a Bausch and Lomb Abbe-3L refractometer which was thermostated at 25°.

Infrared spectra were obtained on Perkin -Elmer Recording Infrared Spectrophotometers, Models 21 and 421, the former being used with a four-fold expanded scale for quantitative measurements.

Nuclear Magnetic Resonance spectra were obtained on Varian Analytical Spectrophotometers, Models A-60 and HR-100.

Solvents

Diethylether: Malinckrodt AR absolute ether was used.

Benzene: Baker and Adamson analytical reagent grade was used.

Pentane: Commercial n-pentane was purified by refluxing with and distillation from phosphorous pentoxide.

Chloroform:

Malinckrodt AR chloroform was purified by shaking twice with concentrated sulfuric acid and then four times with water. A preliminary drying over magnesium sulfate preceded distillation from phosphorous pentoxide. Purified samples were stored in dark tightly stoppered bottles,

and in most instances were used immediately. No samples were used after 48 hours of storage. The centre cut, b.p. 57 - 58° (695mm); n_D^{25} 1.4440 was the fraction always employed. Reported (64) b.p. 58°, n_D^{15} 1.44854.

Sodium methoxide:

A sodium methoxide solution was prepared by addition of the appropriate amount of freshly cleaned sodium to Fisher anhydrous methanol. The resultant solution was standardized against B.D.H. primary standard potassium hydrogen phthalate, using phenolphthalein as indicator. The solution was kept in a tightly-stoppered bottle and showed no change in concentration after two years of storage.

2,6-Lutidine:

Eastman practical grade 2,6-lutidine was dried over potassium hydroxide followed by refluxing with and distillation from barium oxide. The center cut b.p. 139 - 140° (695mm) n_D^{25} 1.4954. was stored over potassium hydroxide pellets in a dark tightly-stoppered bottle. Reported (65) b.p. 143° (760mm), n_D^{25} 1.4953.

Pyridine:

Eastman white Label pyridine was stored over potassium hydroxide in a dark bottle.

Triphenylcarbinol:

Eastman White Label triphenylcarbinol was used without further purification.

2-Methylbenzenesulfinic acid:

This compound was prepared by the method described by Hanke (58) for the preparation of p-chlorobenzenesulfinic acid. In a typical preparation 55 grams (0.52 mole) of o-toluidine was dissolved in 500 ml. water containing 85 ml. concentrated sulfuric acid in a two-litre Erlenmeyer flask equipped with a stirrer. The solution was cooled to below 5° and a solution of 40 grams (0.58 mole) of sodium nitrite in 120 ml. water was added drop-wise with stirring. Sulfur dioxide was bubbled through the solution for a period of from 1 to 2 hours while the temperature was maintained below 5°. Copper powder (200 g.), was added gradually with stirring. The solution was maintained at 5° until after the addition of the copper, but thereafter allowed to warm up to room temperature. Sulfur dioxide addition was continued for an additional hour after addition of copper powder. The mixture was filtered, and the copper mat washed with 20 - 30 ml. of cold water. The acid was then extracted from the copper mat by treatment with 250 ml. of saturated sodium carbonate solution and filtered. The resultant green filtrate was treated with decolorizing charcoal and filtered again. The filtrate was acidified with 50 percent sulfuric acid until no further precipitation of 2-methylbenzenesulfinic acid occurred. The white solid was filtered and washed with about 30 - 40 ml. cold water, then air dried overnight in several layers of absorbent paper towels. A second crop of tan colored crystals was obtained by concentrating the mother liquor. Yield 60 grams (78%), m.p. of white crystals 75 - 76°, m.p. of tan colored crystals 69 - 70°. Reported m.p. 80° (49). Both crops of crystals were used for preparative purposes without further purification.

2-Methylbenzenesulfinyl chloride:

To 12.0 g. (0.078 mole) of 2-methylbenzenesulfinic acid in 40 ml. of pentane was added 19 g. (0.16 mole) thionyl chloride in 30 ml. pentane in a drop-wise manner until evolution of gas subsided. The mixture was filtered through glass wool in a tared 200 ml. filter flask, containing a few drops of thionyl chloride in pentane. Most of the pentane and excess thionyl chloride were removed at the aspirator, and the residue was pumped overnight at the vacuum pump. A yield of 10.5 g. (78%) of yellowish oil was obtained.

Trityl 2-methylbenzenesulfinate (55)

2-Methylbenzenesulfinyl chloride (10.5 g., 0.063 mole) was allowed to react with triphenylcarbinol (10.0 g., 0.038 mole) in the presence of pyridine (88 ml., 1.09 moles). The pyridine solution of triphenylcarbinol was added to the acid chloride in an ice-methanol bath at -15° to -18° , and the mixture was allowed to remain at this temperature for 20 minutes. The reaction flask was then transferred to the freezing compartment of the refrigerator which was maintained at -20° , and allowed to remain there for 4 hours. The contents of the flask were then poured into a one litre beaker filled with ice containing 35 ml. (0.435 mole) concentrated hydrochloric acid, and the mixture was extracted three times with 150 ml. portions of ether. The combined ether extracts were washed once with 150 ml. water and several times with 150 ml. portions of 10% sodium carbonate, until the final sodium carbonate washing was colorless. A final washing with 150 ml. water followed. The ether solution was then dried over

magnesium sulfate in a flask which was cooled with an ice bath at 5°. The ether was removed at the aspirator until the first signs of crystal formation. Subsequent cooling of the ether solution at -20°, yielded ester contaminated with pyridine. The ester contaminated with pyridine was dissolved in cold ether. The excess ether was pumped off at the aspirator until the first signs of crystal formation. At this stage the flask was transferred to the refrigerator and kept at -20° until crystallization was complete. Three such recrystallizations were necessary to obtain pure ester.

If trityl 2-methylphenyl sulfone was present in a sample of ester after work-up, purification was effected by recrystallization from a 50 : 50 mixture of ether-pentane. The compound was dissolved in 50 : 50 ether-pentane at room temperature, and some of the solvent was removed at the aspirator to the first signs of crystal formation. The flask was then placed in a refrigerator at -20° for four hours. The crystals obtained after filtration were found to be rich in sulfone impurity. Concentration of the mother liquor at the aspirator, followed by cooling at -20° overnight, yielded pure ester. The yield of ester in most instances was about 10 g., (67%), m.p. 141 - 144°, (with decomposition). Reported (55) m.p. 138 - 139 (with decomposition). Infrared (CS₂) : 700, 770, 900, 1135 and 3060 cm.⁻¹, n.m.r. (CS₂) : 2.1 (q), 2.7 (m), and τ 7.8 (s), ratio 6.3 : 1 (calculated ratio 6.3 : 1). The following abbreviations are used in the description of n.m.r. spectra : "m" for multiplet, "s" for singlet, "d" for doublet, "t" for triplet and "q" for quartet. Equivalent weight on

hydrolysis 394.5 , calculated 398.5 .

Analysis calculated for:

$C_{26}H_{22}SO_2$:	C, 78.35	H, 5.56
Found	:	C, 78.60	H, 5.49
		78.27	5.51

The compound was stored in the refrigerator at -20° , in a tightly-stoppered flask to prevent decomposition.

Trityl 2-methylphenyl sulfone:

This compound may be conveniently synthesized by refluxing a solution of trityl 2-methylbenzenesulfinate in chloroform (55, 56). However in the first attempted synthesis of trityl 2-methylbenzenesulfinate the only product isolated was the sulfone. Triphenylcarbinol (16.4 g., 0.066 mole), and 2-methylbenzenesulfinyl chloride (23 g., 0.131 mole) were allowed to react in 112 ml. pyridine. After work-up and evaporation of the ether to dryness at the aspirator, 17 g., of crude yellowish crystals contaminated with pyridine were isolated. Two recrystallizations from warm chloroform-ether yielded 12 g. (46%) of white crystals, of trityl-2-methylphenyl sulfone, m.p. $134 - 136^{\circ}$. Reported (55) m.p. $133.5 - 135^{\circ}$. Infrared (CS_2) : 700, 755, 1035, 1120, 1145, 1310 and 3025 cm^{-1} , n.m.r. (CS_2) : 2.8 (m) and τ 8.28 (s), ratio 6. 3 : 1 (calculated ratio 6. 3 : 1).

Trityl benzoate\

This compound was prepared by the method described by von E. Doering (60). Freshly cleaned potassium metal (4 g.) and triphenylcarbinol

(29.2 g., 0.111 mole) were allowed to react in 500 ml. reagent grade xylene in a two-litre 3-necked flask fitted with a stirrer, drying tube, and nitrogen in-take. The mixture was refluxed for 80 hours at which time all the potassium metal had dissolved. The flask was then transferred to an ice-salt-water bath and cooled to 0 to 5°. A 14 g., quantity (0.11 mole) of benzoyl chloride was added by means of a dropping funnel over a period of 40 to 50 minutes. The mixture was filtered and the xylene removed under reduced pressure yielding white crystals, 31 g., (80%) which were then recrystallized from benzene to yield 20 g. (52%) of product, m.p. 169 - 171.4° Lit. (66) 168 - 169°. Infrared (chloroform) 900, 955, 1020, 1070, 1100, 1265, 1310, 1450, 1490, 1595, 1718 and 3028 cm.⁻¹

Analysis calculated for	C ₂₆ H ₂₀ O ₂	:	C, 85.69	H, 5.53
	Found	:	C, 85.55	H, 5.38
			85.85	5.30

Trityl perchlorate:

This salt was prepared by the procedure outlined by Dauben and co-workers (67). Triphenylcarbinol (20 g., 0.077 mole), and perchloric acid (15 ml., 0.16 mole) were allowed to react in 225 ml. acetic anhydride at room temperature to produce 24 g. (87%) of crude trityl perchlorate. Purification was effected by crystallization from a minimum amount of hot acetonitrile to yield 12 g. (44%) of the salt, m.p. 144 - 146°. Literature (67) 143°. The precautions suggested by Dauben in the storage and use of this material were followed.

Trityl p-nitrobenzoate:

Sodium p-nitrobenzoate (14.6 g., 0.08 mole) and trityl perchlorate

(14 g., 0.04 mole) were allowed to react in 150 ml. acetonitrile at room temperature in a 500 ml. Erlenmeyer flask equipped with a stirrer. The contents of the flask were poured into 200 ml. ether and the ether solution washed three times with 100 ml. of water. The ether solution was dried over magnesium sulfate for 15 min., then filtered. The solvent was removed at the aspirator. Two recrystallizations from chloroform-ether yielded 4.39 (26%) of the desired product. Infrared (chloroform), 820, 870, 900, 950, 1010, 1090, 1105, 1265, 1310, 1340, 1440, 1485, 1520, 1600, 1718 and 3028 cm^{-1} .

Analysis calculated for	$\text{C}_{26}\text{H}_{19}\text{O}_4\text{N}$:	C, 76.25	H, 4.68	N, 3.42
	Found	:	C, 76.16	H, 4.86	N, 3.16
			76.20	4.91	

Benzyl 2-methylbenzenesulfinate:

Benzyl 2-methylbenzenesulfinate was prepared by the same method used to prepare benzyl 2,6-dimethylbenzenesulfinate (62). A 6 g. (0.04 mole) quantity of 2-methylbenzenesulfinyl chloride and 2.2 g. (0.02 mole) of benzyl alcohol in 40 ml. of pyridine yielded 3.7 g. (75%) of benzyl 2-methylbenzenesulfinate. The ester was recrystallized from ether. The crystals melted when allowed to warm up to room temperature. Infrared (CS_2), 700, 720, 760, 910, 935, 1140, 1200, 1370, 2925, 3020 and 3035 cm^{-1} , n.m.r. (CS_2) 2.15 (q) 2.8 (m) 5.32 (d) 5.55 (d) ($J_{AB} = 11.5$ cps) and τ 7.68 (s) ratio 1 : 1.5 : 4.6 (calculated ratio 1 : 1.5 : 4.5). Equivalent weight on hydrolysis in methyl alcohol-water containing sodium methoxide with potassium hydrogen phthalate as the standard acid and phenolphthalein as indicator, found 246.3, (calculated : 246.3).

Analysis calculated for $C_{14}H_{14}SO_2$: C, 68.27 H, 5.69
Found : C, 68.03 H, 5.62
 68.03 5.66

Benzyl azide;

Benzyl azide was prepared by the method described by Curtius and Ehrhart (74). A 20 g., (0.158 mole) quantity of benzyl chloride, and 15 g. sodium azide in 45 ml. absolute ethanol yielded 16 g. (73%) of the desired product, b.p. $71 - 72^{\circ}$ at 9.5 mm., n_D^{25} 1.5342, (reported (74) b.p. 82.5° at 16.5 mm., n_D^{25} 1.53414): infrared (CCl_4) 705, 1255, 2104, and 3010 cm^{-1} n.m.r. (CCl_4) 2.70 (s) and 5.76 (s), ratio 1 : 2.50 (calculated ratio 1 : 2.50).

Tetra-n-butylammonium bromide;

1-Bromobutane (137 g., 1 mole) and tributylamine (185 g., 1 mole) were heated in a 500 ml. round-bottom flask on the steam bath for 14 days. The resulting dark red oil was dissolved in ethyl acetate-pentane and the resulting mixture placed in the refrigerator. The crystals which formed were separated by filtration and recrystallized once from ethyl acetate-pentane and twice from ethyl acetate to yield 180 g. (56%) white crystals; m.p. $102.5 - 103.5^{\circ}$. Reported (68) m.p. $102.7 - 103.5$.

Tetra-n-butylammonium hydroxide;

Silver nitrate (28 g., 0.162 mole) was dissolved in 200 ml. of water and a 30% sodium hydroxide solution added until the solution was strongly basic. The resultant black precipitate was washed by decantation with distilled water until the final water washing was neutral to litmus

paper. The excess water was poured off. The silver oxide suspension was then added to a water solution (200 ml.) of 40 g. (0.125 mole) tetrabutylammonium bromide with stirring. When the solution tested negative to halide ion the silver salt was filtered off.

Tetra-n-butylammonium benzoate:

Tetra-n-butylammonium bromide 45 g. (0.14 mole) was used to prepare the hydroxide in 60% ethanol by the procedure described above. Benzoic acid was added to a stirred solution of the hydroxide until the reaction solution showed a pH of 8. Most of the ethanol and water were removed at the aspirator. The flask containing the residual yellow oil was stored under reduced pressure in a vacuum dessicator over phosphorous pentoxide until the compound was dry and solid. The crude solid obtained was recrystallized three times from ethyl acetate to give 40 g. (79%) of white crystals, m.p. 60 - 62°. Molecular weight determination by titration in acetic acid using a standard solution of perchloric acid in glacial acetic acid to the green end point of p-naphtholbenzein, found 361.8, calculated 363.3. Infrared (nujol) 710, 1365, 1455, 1475, 1550, 1590 and 2920 cm.⁻¹, n.m.r. (D₂O), 2.1 (q), 2.6 (m) 7.1 (m) and 7.8 (m), ratio 1 : 7.1 (calculated ratio 1 : 7.2). Satisfactory analysis could not be obtained for this compound.

Analysis calculated for	$C_{23}H_{41}O_2N$:	C, 75.98	H, 11.37	N, 3.85
	Found	:	C, 74.60	H, 11.24	N, 3.98
			74.53	10.95	3.79

Tetra-n-butylammonium p-nitrobenzoate:

The same procedure used for preparing the benzoate salt was employed

for the preparation of tetra-n-butylammonium p-nitrobenzoate. A 45 g. (0.14 mole) quantity of tetra-n-butylammonium bromide yielded 25 g. (44%) of purified yellow crystals of tetra-n-butylammonium p-nitrobenzoate, m.p. 124 - 125°. Molecular weight determination by titration in acetic, acid found 406.1, calculated 408.6. The infrared spectrum (nujol) 730, 800, 880, 1095, 1320, 1490, 1580, 1610 and 2910 cm^{-1} ; n.m.r. (D_2O); 2.0 (s), 7.0 (m) and τ 8.8 (m) ratio 1 : 9.05 (calculated ratio 1 : 9.00).

Analysis calculated for	$\text{C}_{23}\text{H}_{40}\text{O}_4\text{N}_2$:	C, 67.61	H, 9.79	N, 6.86
	Found	:	C, 67.39 67.17	H, 9.97 9.83	N, 7.08

Control on the isolation of trityl benzoate in chloroform in the presence of tetra-n-butylammonium benzoate and 2,6-lutidine (Run 3-45)

Trityl benzoate (0.2106 g., 0.0121 M.) and tetra-n-butylammonium benzoate (1.8750 g., 0.1031 M.) were weighed into a 50 ml. volumetric flask, and chloroform containing 0.0347 M. 2,6-lutidine was added to the mark. The contents of the flask were shaken 100 times then poured into a separatory funnel containing 50 ml. chloroform and 100 ml. water. The volumetric flask was rinsed twice with 25 ml. portions of chloroform and these washings also added to the separatory funnel. After each of 9 extractions with 100 ml. water, the aqueous layer was discarded. The chloroform layer was transferred to a 250 ml. Erlenmyer flask, and dried over magnesium sulfate for 25 minutes. The solvent, after filtration, was evaporated at the aspirator. The oily residue was then stored under reduced pressure in a vacuum dessicator containing phosphorous pentoxide until a

dry solid (0.2003 g.) was obtained. Chloroform (50 ml.) was then added by means of a calibrated automatic pipette.

An aliquot of the chloroform solution was transferred to a 0.5mm. cell which was previously matched against a variable spacer reference cell to compensate for any absorbance due to the solvent. Using a Perkin Elmer Model 21 Spectrophotometer, at a 20cm. per micron scale setting, and scanning from 1800 - 1640 cm^{-1} , the absorbance due to the carbonyl stretching vibrations at 1718 cm^{-1} , for trityl benzoate was determined. From the absorbance, the concentration of trityl benzoate was obtained from the plot of absorbance against concentration.

Product run on trityl 2-methylbenzenesulfinate with tetra-*n*-butylammonium benzoate in chloroform containing 2,6-lutidine at 25⁰. Run 3-56

Trityl 2-methylbenzenesulfinate (0.4339 g., 0.02178 M.), (containing 7% trityl 2-methylphenyl sulfone as an impurity), and tetra-*n*-butylammonium benzoate (3.5130 g., 0.19324 M.) were weighed into a 50 ml. volumetric flask and chloroform containing 0.0356 M. 2,6-lutidine was added to the mark. The flask was stoppered, shaken 100 times and placed in a 25⁰ thermostated water bath for 4 hours, (the time estimated for 10 half-lives for the reaction of the ester). The extraction procedure was identical to that described for the control runs. A 0.4263 g. quantity of dry residue was isolated, and to this 25 ml. of chloroform was added with a calibrated 25 ml. automatic pipette. The absorbance due to trityl benzoate at 1718 cm^{-1} , was determined by scanning the region 1800 - 1640 cm^{-1} , as described previously. From a plot of the relationship of concentration and absorbance for trityl

benzoate in chloroform. it was estimated that a 29.4% yield of trityl benzoate was obtained. Corrections for the presence of 7% sulfone in the starting ester and 90% recovery of trityl benzoate as dictated by the control runs gave the absolute amount of trityl benzoate produced as 35%.

Quantitative analysis of trityl 2-methylbenzenesulfinate by infrared analysis

Trityl 2-methylbenzenesulfinate (0.1034 g., 0.02595 M.) was weighed in a 10 ml. volumetric flask, and carbon disulfide added to the mark. A portion of the solution was transferred to a 0.5mm. sodium chloride cell and the absorbance due to trityl 2-methylphenyl sulfone at 1310 cm^{-1} , determined by use of the Perkin Elmer Model 21 Spectrophotometer. A variable spacer cell previously blanced against the sample cell was used to compensate for any absorbance due to the solvent. An absorbance of 0.07142 indicated the presence of 6.53% sulfone in the above sample of ester.

Lambert-Beer Law determinations

The procedure used for the Lambert-Beer law determinations for trityl benzoate and trityl p-nitrobenzoate was identical.

Trityl benzoate in chloroform

Trityl benzoate (0.4983 g. 0.02860 M.) was weighed in a 50 ml. volumetric flask and purified chloroform containing 0.035 M. 2,6-lutidine was added to the mark. Using a 5 ml. calibrated automatic pipette 20, 15, and 10 ml. of the above solution were transferred to 25 ml. volumetric flasks and chloroform solution added to the mark, thereby allowing the preparation

of 80, 60, and 40% solutions of trityl benzoate. Using the same 5 ml. pipette, 5 ml. of the 40% trityl benzoate solution was transferred to a 10 ml. volumetric flask and chloroform solution added to the mark. For the preparation of a 10% solution 5 ml. of the 20% solution was diluted to 10 ml. in a volumetric flask. Samples of these solutions were then successively transferred to a 0.5mm. sodium chloride cell, which was previously balanced against a variable spacer reference cell to compensate for any absorbance due to the solvent. Using a Perkin Elmer Model 21 Spectrophotometer, at a 20cm. per micron scale setting, and scanning the region $1800 - 1640 \text{ cm}^{-1}$ the absorbance of the carbonyl band at 1718 cm^{-1} , for trityl benzoate was determined. Table III and Figure II, show the results of such a determination.

Lambert-Beer Law determination of trityl 2-methylphenyl sulfone in carbon disulfide

Trityl 2-methylphenyl sulfone (0.0985 g. , $9.98 \times 10^{-3} \text{ M.}$) was weighed in a volumetric flask and carbon disulfide added to the mark. Using a 5 ml. automatic pipette 5 ml. of the solution was transferred to a 10 ml. volumetric flask and carbon disulfide added to the mark. With the use of the same automatic pipette 5 ml. of the latter solution was transferred to a 10 ml. volumetric flask and carbon disulfide added to the mark. Samples of these solutions were then successively analysed by quantitative infrared methods, as described previously. The region $1370 - 1230 \text{ cm}^{-1}$, was scanned and the absorbance at 1310 cm^{-1} , calculated. The results are listed in Table IX and a plot of the relationship between absorbance and concentration is given

in Figure VII.

TABLE IX

THE RELATIONSHIP BETWEEN OPTICAL DENSITY AND CONCENTRATION OF TRITYL 2-METHYL-PHENYL SULFONE IN CARBON DISULFIDE AT 1310 cm^{-1}

Concentration $\text{m/l} \times 10^3$	I_0/I	$\text{Log } I_0/I$
9.89	2.256	0.3533
4.95	1.536	.1864
2.48	1.238	.0926

Lambert Beer Law determination of Benzyl azide in Chloroform

Benzyl azide (556.3 mg) was weighed in a 100 ml. volumetric flask and chloroform added to the mark. A 5 ml. automatic pipette was used to transfer 20, 15, 10, and 5 ml. quantities respectively to 25 ml. volumetric flasks which were filled to the mark with chloroform. Samples of these solutions were then successively subjected to quantitative infrared analysis in a manner similar to that described previously. The region $2200 - 2000\text{ cm}^{-1}$, was scanned and the absorbance at 2104 cm^{-1} , determined. Figure IV and Table VII show the results of such determinations.

Kinetic procedure

Benzyl 2-methylbenzenesulfinate (0.1270 g., 0.03815 M.) was weighed in a 25 ml. volumetric flask and a standard chloroform solution of tetrabutyl-

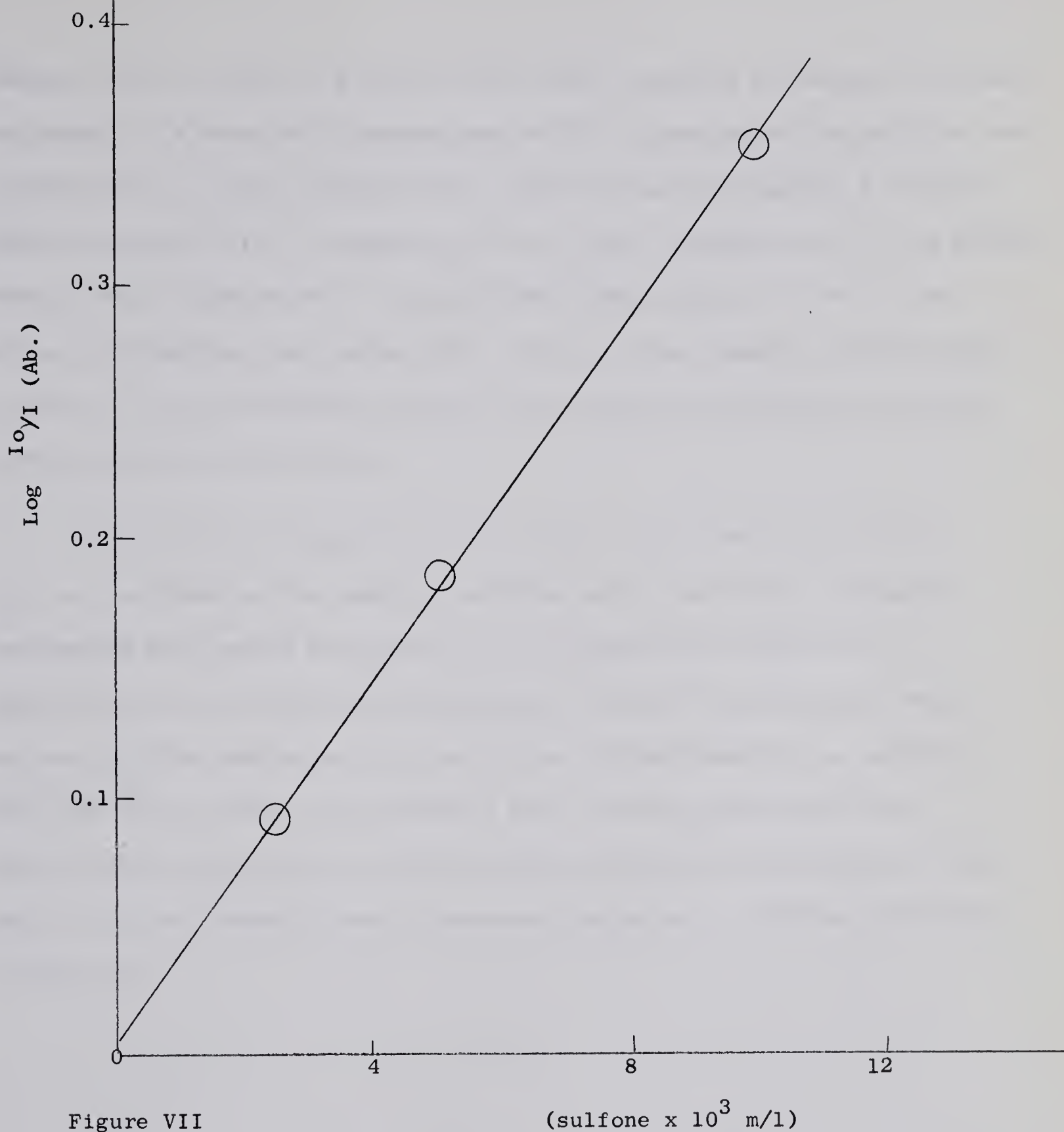


Figure VII

Relationship between optical density and concentration for
trityl 2-methylphenyl sulfone in carbon disulfide at 1310 cm.⁻¹

ammonium azide (0.06231 M.) added to the mark. The flask was shaken 100 times and placed in a water bath thermostated at 25⁰. A portion of the solution was transferred to a sodium chloride cell previously matched against a variable spacer reference cell to compensate for any small absorbance due to the solvent. Using a Perkin Elmer Model 21 Infrared Spectrophotometer at a 20 cm. per micron scale setting the region 2200 - 2000 cm.⁻¹, was scanned. The absorbance at 2104 cm.⁻¹, was determined and the first-order rate constants calculated from the observed absorbances.

Due to the slow nature of this reaction after twenty-four hours ca. 3 ml. portions of the reaction solution were transferred to ampoules. The ampoules were sealed and placed in the thermostated water bath. At appropriate intervals the sealed tubes were removed from the bath, opened and the solutions subjected to quantitative infrared analysis as described. After the kinetic data were recorded a total infrared spectrum of the solution was taken, in order to qualitatively check the disappearance of the band at 1140 cm.⁻¹ Benzyl 2-methylbenzenesulfinate has an intense absorption at 1140 cm.⁻¹

CHAPTER II

The reaction of Trityl 2-methylbenzenesulfinate with various Quaternary Ammonium salts in acetonitrile.

INTRODUCTION

To gain further information on the mechanism of the rearrangement reaction of trityl 2-methylbenzenesulfinate in acetonitrile, the effect of the common ion salt tetra-n-butylammonium 2-methylbenzenesulfinate, and the effects of non-common ion salts such as tetra-n-butylammonium perchlorate, azide and 2,6-dimethylbenzenesulfinate were studied. In this chapter the consequences of the addition of these salts are reported.

RESULTS

Preparations

The syntheses of trityl 2-methylbenzenesulfinate and trityl 2-methylphenyl sulfone were described in detail in Chapter I. In an analogous manner triphenylcarbinol and 2,6-dimethylbenzenesulfinyl chloride in pyridine afforded after work-up trityl 2,6-dimethylbenzenesulfinate. The infrared spectrum showed strong absorbing bands at 700, 770, 900 and 1135 cm^{-1} , the latter a characteristic region for sulfinate ester absorption (59). Nuclear magnetic resonance signals appeared at τ 2.5 - 3.2 (complex multiplet) and τ 7.2 (singlet). The former is a region for aromatic proton signals, and the latter is associated with the protons of the methyl groups substituted on the benzene ring. The calculated ratio of aromatic to methyl protons is 3 : 1,

found 3.05 : 1.

Trityl azide was prepared by the method described by Swain (13) which consisted of allowing trityl isothiocyanate (55) to react with sodium azide in acetone-water. After work-up trityl azide was isolated. The infrared spectrum (carbon disulfide), showed intense bands at 700, 750, 1250 and 2100 cm^{-1} . The latter band has been identified (59) as being characteristic of $\text{N} \equiv \text{N}$ absorption of azide.

Ultraviolet measurements at 283 mu.

In studying the rate of rearrangement of trityl 2-methylbenzenesulfinate to the sulfone in chloroform, it is possible to follow the appearance of the sulfone band at 1310 cm^{-1} , (55). However in acetonitrile, it is not possible to follow the appearance of this band, since acetonitrile absorbs strongly in this region. In the ultraviolet, trityl 2-methylphenyl sulfone absorbs at 283 mu., and it is possible to make kinetic measurements by following the change in absorbance with time at this wavelength. Trityl 2-methylbenzenesulfinate ($\epsilon = 676$). also absorbs at this wavelength.

From the absorbance values recorded at 283 mu the first-order rate constants were calculated by means of the equation:

$$k = \frac{2.303}{t} \log \frac{(A_{\infty} - A_0)}{(A_{\infty} - A)}, \text{ where } A \text{ is the absorbance at}$$

any time t , A_0 is the absorbance at time t_0 , and A_{∞} is the absorbance recorded at the end of the reaction.

The rate constants are based on "experimental infinity", values, and measure the total rate of reaction. Generally the reactions were followed to about 90 - 95% completion. The percentage infinity was obtained by dividing the observed infinity by the theoretical infinity. This afforded an additional check on the purity of the substrate. All infinity points were averages of at least 4 points taken between 10 and 100 half-lives of the reaction.

To determine the relationship between optical density and concentration for trityl 2-methylphenyl sulfone in acetonitrile at 283 mu, an accurately weighed amount of sulfone was dissolved in purified acetonitrile. Quantitative dilutions of this solution were effected by use of an automatic pipette. The absorbance of these solutions at 283 mu. were recorded, and plotted against the concentration of sulfone. A linear relationship is observed in the concentration range employed. These results are given in Table X and Figure VIII.

TABLE X

THE RELATIONSHIP BETWEEN OPTICAL DENSITY AND CONCENTRATION FOR TRITYL 2-METHYL-PHENYL SULFONE IN ACETONITRILE AT 283 mu.

(Sulfone) mg./ml.	Absorbance
.532	1.921
.333	1.218
.251	0.980
.201	.805
.125	.488
.0627	.238
.0314	.117

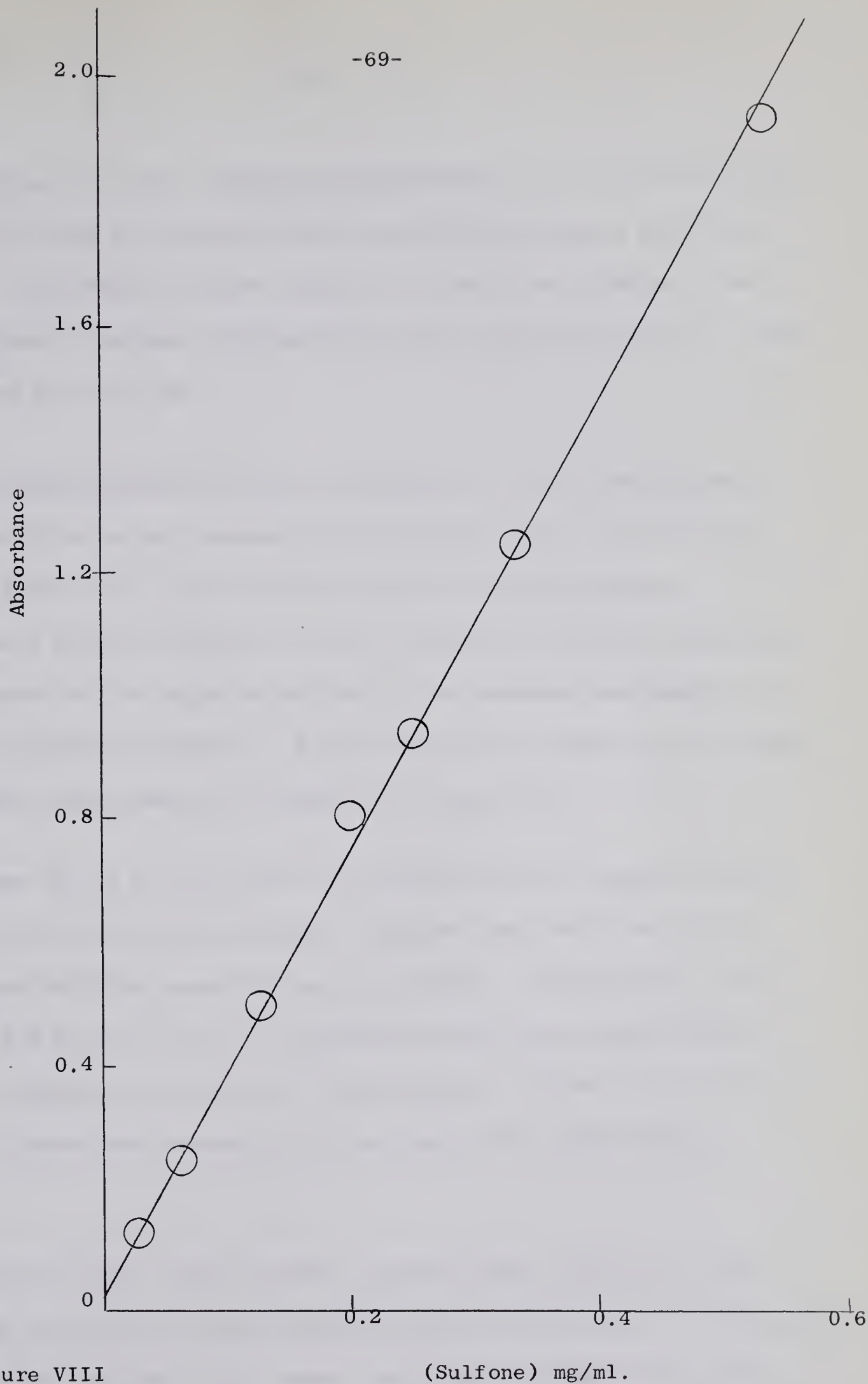


Figure VIII

(Sulfone) mg/ml.

The relationship between optical density and concentration
for trityl 2-methylphenyl sulfone in acetonitrile at 283 mμ.

The reaction of trityl 2-methylbenzenesulfinate in acetonitrile in the presence of 2,6-lutidine and tetrabutylammonium perchlorate gave good first-order kinetics. There were no drifts apparent in the first-order rate constants, and duplicate runs were reproducible within experimental error. Average deviations are ca. 2 to 5%.

Trityl 2-methylbenzenesulfinate rearranges to trityl 2-methylphenyl sulfone in acetonitrile in the presence of 2,6-lutidine with a first-order rate constant of $5.76 \times 10^{-4} \text{ sec}^{-1}$. The addition of tetrabutylammonium perchlorate causes a linear increase in rate. A summary of the rate constants for the rearrangement of the ester to sulfone in the presence and absence of perchlorate salt is given in Table XI. A plot of the first-order rate constants against perchlorate concentration is presented in Figure IX.

An increase in the 2,6-lutidine concentration has no apparent effect on the observed first-order rate constants, (Compare runs 3-288 and 4-6 of Table XI). At a 2,6-lutidine concentration of 0.0282 M a first-order rate constant of $7.87 \pm 0.25 \times 10^{-4} \text{ sec}^{-1}$ was obtained. When the concentration of the base was increased to 0.05700 M a rate constant of $8.06 \pm 0.42 \times 10^{-4} \text{ sec}^{-1}$, was found. These rate constants are the same within experimental error.

Tables XII and XIII, present sample reaction rates. Table XII shows the results of the reaction of trityl 2-methylbenzenesulfinate with 2,6-lutidine in acetonitrile at 25° and Table XIII shows the effect of added tetra-n-butylammonium perchlorate on the rate of rearrangement of the ester. Figure X and XI, show the relationship between $\log (A_{\infty} - A)$ and time for runs 3-282 and

TABLE XI

THE REARRANGEMENT OF TRITYL 2-METHYLBENZENESULFINATE WITH TETRABUTYLAMMONIUM PERCHLORATE AND 2,6-LUTIDINE IN ACETONITRILE AT 283 mu. AT 25.15 ± 0.15^a

Run	(Ester)M. $\times 10^3$	(ClO ₄ ⁻) M	(2,6-lut.)	$k_1 \times 10^4 \text{ sec}^{-1}$
3-279	3.653	-	0.02810	5.76 ± 0.12
3-282	0.792	-	.02829	5.80 ± 0.12
3-290	1.2998	0.01381	.03135	6.19 ± 0.18
3-284	0.918	.06032	.02829	7.41 ± 0.20
3-288	1.1643	.06904	.05700	8.06 ± 0.42
4-6	1.360	.07000	.02815	7.87 ± 0.25
3-292	1.1994	.09595	.02601	7.90 ± 0.23
4-4	1.1568	.10038	.02815	8.13 ± 0.42

a - The temperature as recorded here is the actual temperature of the reaction solution in the cell determined by a thermocouple. The cell compartment was kept at a constant temperature with the aid of a water bath thermostated at $25.10 \pm 0.02^\circ$.

3-284. Both plots show excellent linearity. The results of Table XII and XIII, together with the plots of Figure X and XI, show that there is no drift in the observed first-order rate constants.

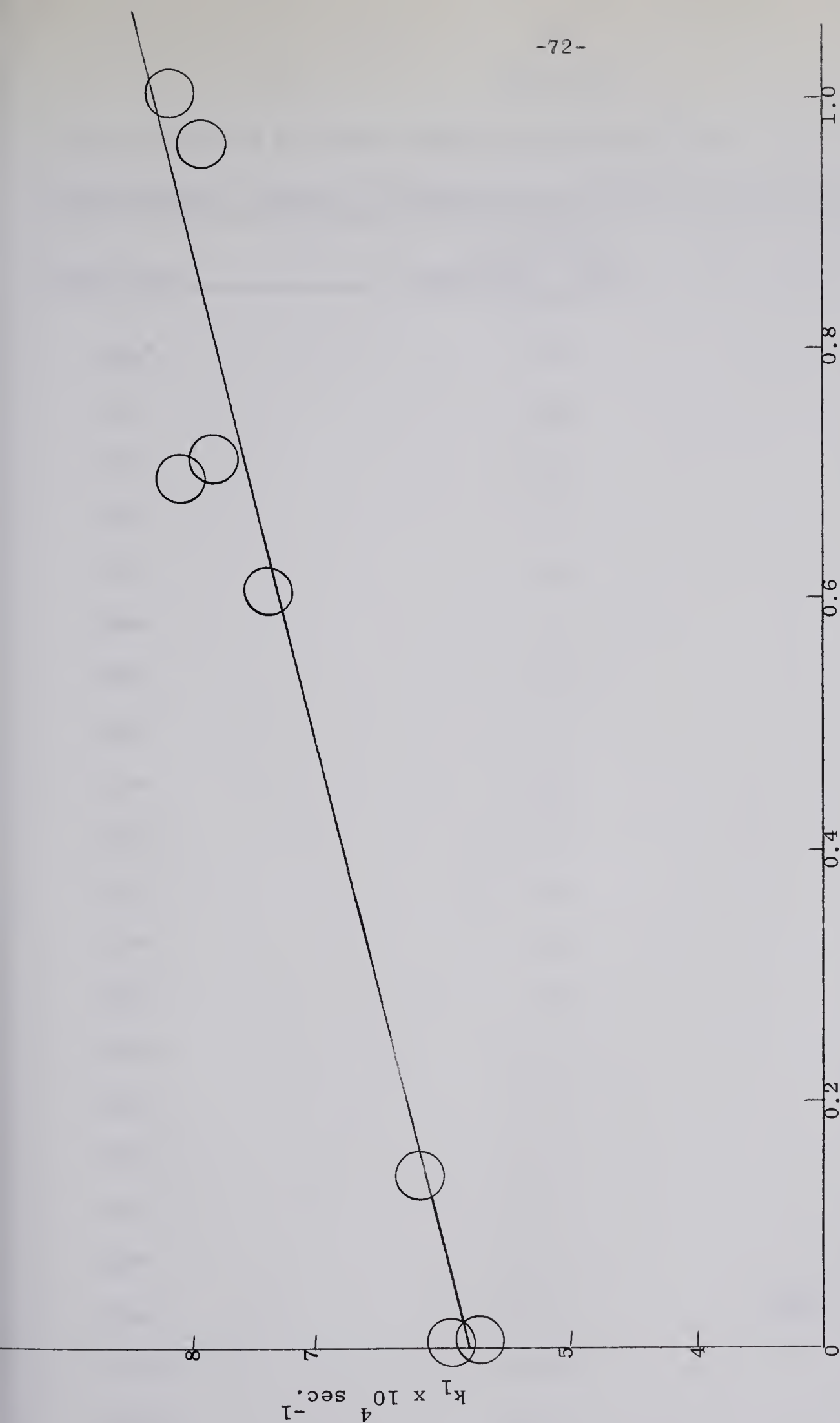


Figure IX

10 (Tetrabutylammonium perchlorate) M

Relationship between the first-order rate constant obtained and the concentration of perchlorate salt added in the rearrangement of trityl 2-methylbenzenesulfonate to sulfone in acetonitrile.

TABLE XII

RATE OF REACTION OF TRITYL 2-METHYLBENZENESULFINATE (7.921×10^{-4} M) WITH
 2,6-LUTIDINE (0.02839 M) IN ACETONITRILE AT 283 μ AT $25.15 \pm .15^\circ$. RUN 3-282

Time (sec)	Absorbance		$k_1 \times 10^4_{-1}$ sec
	Observed	(Aob)	
0	0.582		-
226 ^a	.642		-
303	.669		(6.55)
373	.688		5.78
457	.711		5.65
542	.728		(5.32)
658	.767		5.93
859	.820		6.05
1027	.850		5.80
1191	.882		5.82
1353	.919		6.10
1527	.935		5.75
1720	.968		5.88
1862	.990		5.96
2062	1.02		6.20
2412	1.04		5.81
2818	1.07		5.87
3448	1.13		(6.56)
4287	1.14		(5.48)
7088	1.18		Avg = 5.89 ± 0.12
10573	1.18		
13565	1.20		
22863	1.23		
74851	1.23		

(a) Used as zero time in the rate calculation.

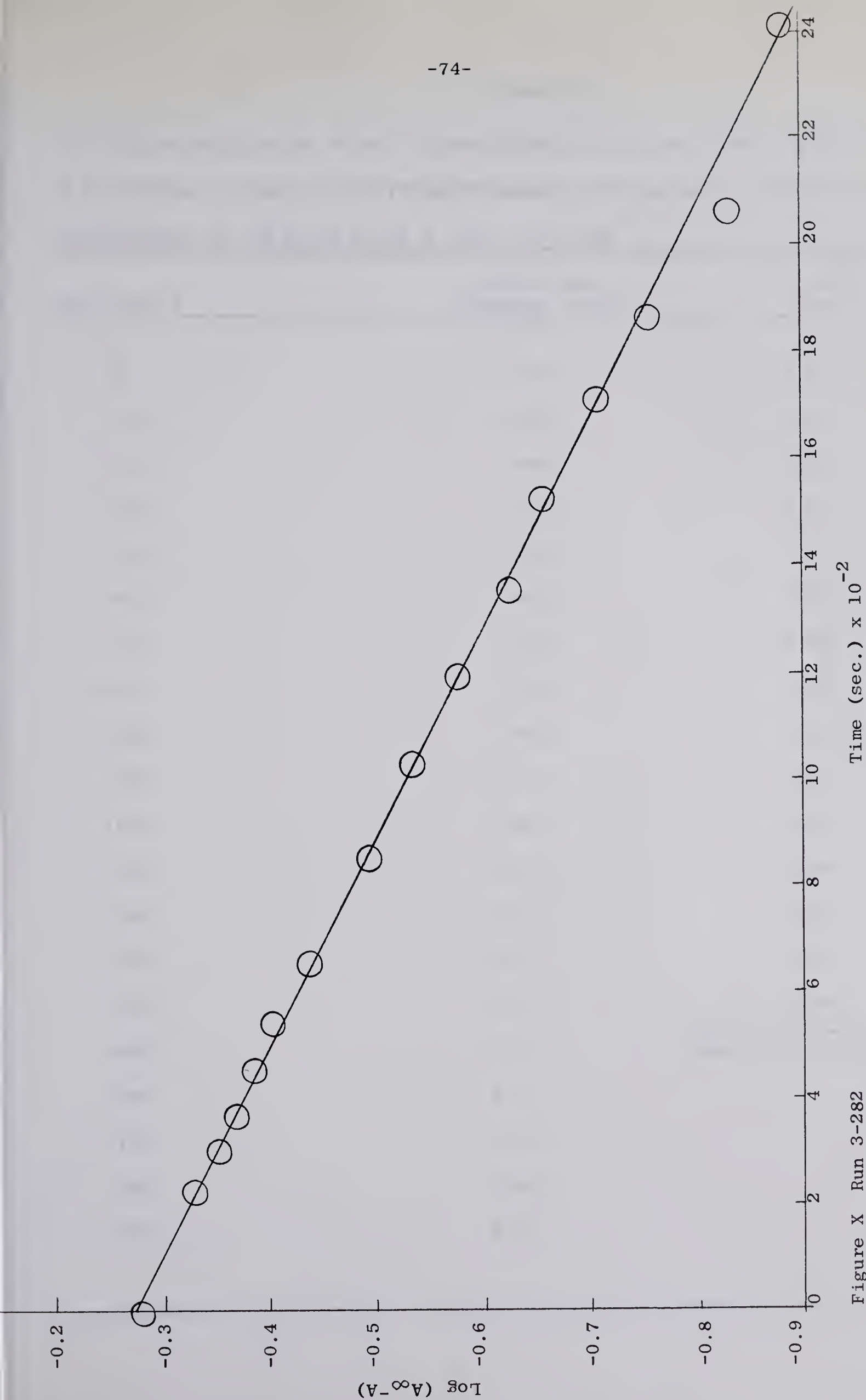


Figure X Run 3-282

The relationship between $\log (A_{\infty} - A)$ and time for the reaction of trityl 2-methylbenzenesulfinate with 2,6-lutidine in acetonitrile at $25.15 \pm 0.15^{\circ}\text{C}$.

TABLE XIII

THE RATE OF REACTION OF TRITYL 2-METHYLBENZENESULFINATE (9.180×10^{-4} M) WITH
 2,6-LUTIDINE (0.02829 M) AND TETRABUTYLAMMONIUM PERCHLORATE (0.06032 M) IN
 ACETONITRILE AT 283 mu AT $25.15 \pm .15^{\circ}$. RUN 3-284

Time (sec.)	Absorbance Observed (Aob)	$k_1 \times 10^4$ sec ⁻¹
0	0.617	-
78	.654	7.65
168	.693	7.68
373	.768	7.32
503	.815	7.75
603	.843	7.40
747	.883	7.40
822	.889	(6.93)
951	.932	7.38
1218	.982	7.25
1372	1.02	7.64
1613	1.06	7.68
1869	1.08	7.26
2348	1.12	7.10
3032	1.17	7.30
4162	1.18	(5.38)
6543	1.24	Avg. = 7.41 ± 0.20
7498	1.23	
11371	1.24	
73501	1.26	
94793	1.25	

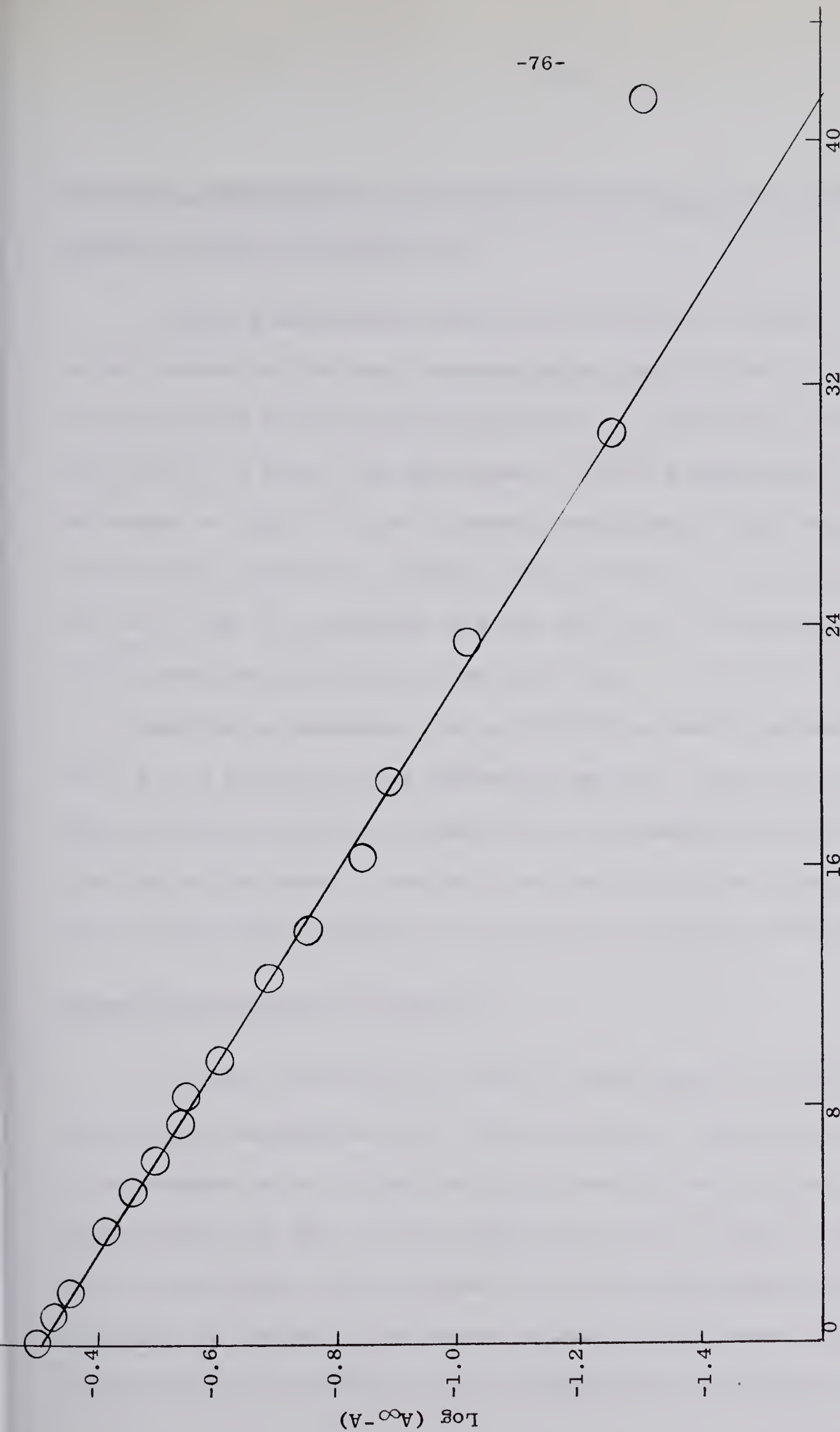


Figure XI Run 3-284

The relationship between $\log(A_{\infty} - A)$ against time for the reaction of ester with 2,6-lutidine in the presence of perchlorate salt in acetonitrile at $25.15 \pm .15^{\circ}$.

Concurrent Rearrangement and Exchange Reactions of Trityl 2-methylbenzenesulfinate in Acetonitrile.

Trityl 2-methylbenzenesulfinate was allowed to react in acetonitrile in the presence of tetrabutylammonium azide, perchlorate, 2-methylbenzenesulfinate and 2,6-dimethylbenzenesulfinate. In acetonitrile solvent it is not possible to follow the appearance of trityl 2-methylphenyl sulfone absorbance at 1310 cm^{-1} , due to strong absorption in this region by the solvent, as previously pointed out. However trityl azide has an intense absorbance at 2100 cm^{-1} , and it is possible to study the rate of disappearance of the ester by following the appearance of the azide band at 2100 cm^{-1} , a region where it is possible to compensate for any absorbance due to acetonitrile with the aid of a variable spacer reference type cell. This is the original method used for studying the concurrent rearrangement and substitution reactions of the ester in acetonitrile. The ultraviolet measurements of the rate were later employed to complement the infrared measurements.

Infrared measurements at 2100 cm^{-1}

The rate constants are based on "experimental infinity", values and therefore measure the total rate of reaction. From the absorbance of the samples after at least ten half-lives for the reaction, the concentration and thus the percentage trityl azide formed in the reaction could be calculated. This was done in the following manner. From the absorbance at "infinity" the concentration of trityl azide is determined from the plot of absorbance against concentration. Dividing the concentration

of trityl azide by the concentration of starting ester gave the fraction of trityl azide produced. The percentage sulfone may be obtained by subtracting the percentage azide from 100.

To determine the relationship between optical density and concentration, standard solutions of trityl azide were prepared in purified acetonitrile, and the optical density of these solutions were determined at 2100 cm^{-1} . The relationship between optical density and concentration for trityl azide in acetonitrile is given in Table XIV and Figure XII. The relationship is not linear.

TABLE XIV

THE RELATIONSHIP BETWEEN OPTICAL DENSITY AND CONCENTRATION FOR TRITYL AZIDE IN ACETONITRILE AT 2100 cm^{-1}

Trityl azide mg./ml.	Log I_0/I
7.36	0.8612
5.52	.7501
3.68	.5715
2.76	.4337
1.84	.3156
1.38	.2326
.69	.1208

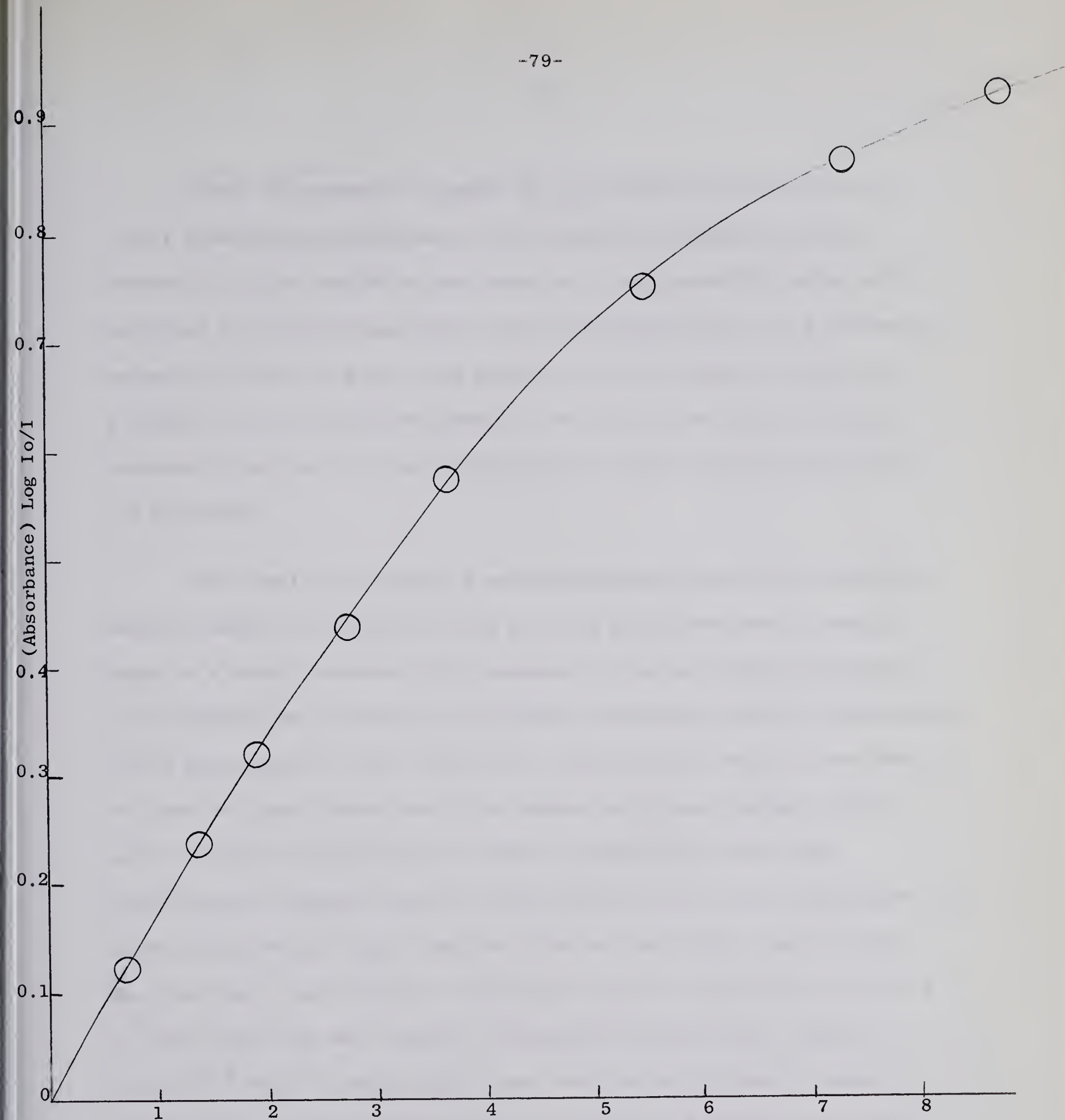


Figure XII

(Trityl azide) mg/ml

The relationship between optical density and concentration for Trityl azide in acetonitrile at 2100 cm.⁻¹

Table XV presents a summary of the results of the reaction of trityl 2-methylbenzenesulfinate with tetra-n-butylammonium azide in acetonitrile. The results of the reaction of the ester with azide salt, and added tetra-n-butylammonium 2-methylbenzenesulfinate and 2,6-dimethylbenzenesulfinate salts are also summarized in this table. In Table XXI a summary of the results obtained for the reaction of trityl 2-methylbenzenesulfinate with tetra-n-butylammonium azide and perchlorate salts are presented.

The reaction of trityl 2-methylbenzenesulfinate with tetrabutylammonium azide in acetonitrile did not give good first-order kinetics. There is a steady downward drift apparent in the calculated first-order rate constants as the reaction progresses. Duplicate runs are reproducible within experimental error. (Table XV, runs 3-214 and 3-224). About 58% of the reaction under these conditions appear to be rearrangement of the ester to trityl 2-methylphenyl sulfone accompanied by about 42% substitution. A sample reaction rate is shown in Table XVI, and Figure XIII, shows a plot of $\log (C_{\infty}-C)$ against time for run 3-224. From this plot the first-order rate constant calculated from the initial slope is $9.35 \times 10^{-4} \text{ sec.}^{-1}$, and the rate constant calculated from the final slope is $7.58 \times 10^{-4} \text{ sec.}^{-1}$. In this example the reaction was followed to about 97% completion and the infinity was an average of 4 points taken after 10 half-lives of the reaction had elapsed. The percent of trityl azide produced in the reaction was obtained by dividing the observed infinity by the theoretical infinity and was found in duplicate runs 3-214 and

TABLE XV

THE REARRANGEMENT AND SUBSTITUTION OF TRITYL 2-METHYLBENZENESULFINATE WITH
SOME TETRABUTYLAMMONIUM SALTS IN ACETONITRILE AT $25.23 \pm .24^{\circ}$.^(c)

Run	(Ester) M	(N ₃ ⁻) M	(2-salt) ^(c) M	(2,6-salt) ^(d) M	$k \times 10^4$ sec ⁻¹	F _{azide}
3-214	0.01925	0.06409	-	-	9.65 ^a 9.43 \pm .50	0.42
3-222	.02098	"	-	0.10870	8.58 ^a	.42
3-224	.02033	"	-	-	9.35 ^a 9.16 \pm .35	.41
3-226	.02040	"	0.10951	-	8.58 ^a 8.41 \pm .51	.29
3-236	.02017	"	.10997	-	8.85 ^a 8.57 \pm .30	.27
3-230	.02000	"	-	.10742	8.67 ^a	.40
3-240	.01950	"	.10713	-	8.85 ^a 8.84 \pm .20	.28
3-242	.02068	.06715	-	.23172	7.70 ^a	.40
3-258	.02073	.06364	-	.23124	7.80 ^a	.41
3-262	.02211	.06364	.24400	-	7.99 ^a 7.82 \pm .30	.18
3-264	.02574	.06364	.21910	-	7.88 ^a 7.66 \pm .31	.18

(a) - These values are calculated from plots of $\log (C_{\infty} - C)$ against time using the initial slopes, in the case of drifting rates or the slope of the line in other instances.

(b) - The temperature recorded here is the actual temperature of the reaction solution. The cell containing the reactants was stored in a Barnes Engineering Model 104 sealed cell thermostated at 25° . The temperature of the cell solution was obtained with the aid of a copper-constantan thermocouple.

(c) - Tetrabutylammonium 2-methylbenzenesulfinate.

(d) - Tetrabutylammonium 2,6-dimethylbenzenesulfinate.

TABLE XVI

RATE OF REACTION OF TRITYL 2-METHYLBENZENESULFINATE (0.02033 M.) WITH TETRA-BUTYLAMMONIUM AZIDE (0.06409 M,) IN ACETONITRILE AT 2100 cm^{-1} AT $25.23 \pm .24^\circ$
 RUN 3-224

Time (sec.)	Log I ₀ /I	Cob mg/ml	k x 10 ⁴ sec. ⁻¹
0	0.0767	0.41	-
105	.1103	.60	9.75
296	.1550	.90	9.75
421	.1805	1.04	9.28
597	.2134	1.23	9.15
714	.2305	1.34	9.10
794	.2487	1.45	9.61
921	.2584	1.49	8.80
1096	.2827	1.62	8.88
1264	.2961	1.73	8.97
1525	.3136	1.82	8.32
1801	.3275	1.91	(8.15)
2177	.3454	2.02	(8.05)
2784	.3578	2.12	(7.54)
3760	.3819	2.28	8.50
5307	.3843	2.30	(6.57)
7200	.3915	2.36	Avg = 9.16 ± .35 ^a
11460	.3908	2.35	
14760	.3945	2.37	
46560	.3913	2.35	

a - Rate constants indicated in brackets were omitted in calculating the average.

C_∞ = 2.36 mg.ml. = 41% Trityl azide of theoretical

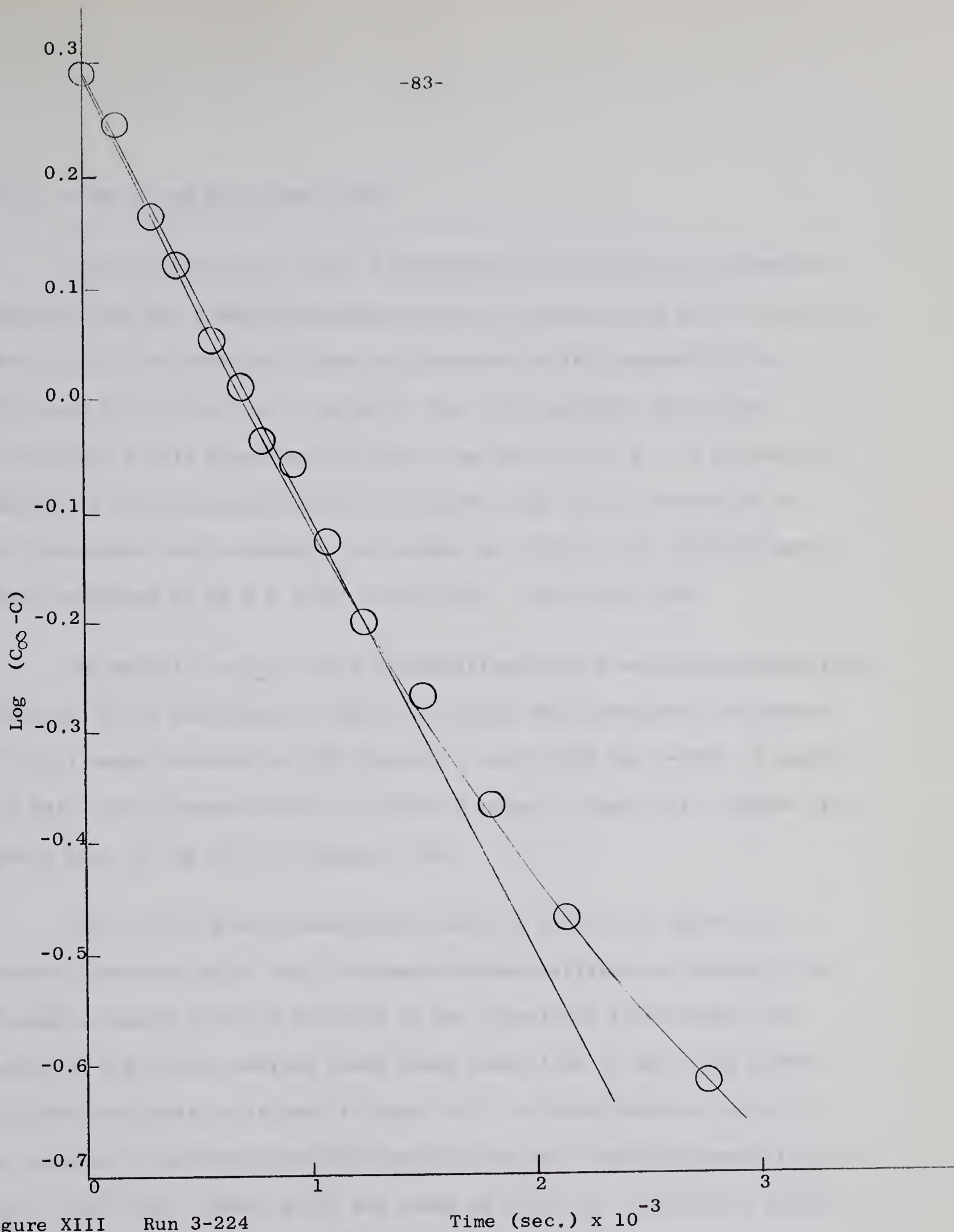


Figure XIII Run 3-224

Relationship between $\log (C_{\infty} - C)$ against time for the reaction of trityl 2-methylbenzenesulfinate with azide salt in acetonitrile.

3-224, to be 42 and 41% respectively.

In the reaction of trityl 2-methylbenzenesulfinate with tetrabutylammonium azide and 2-methylbenzenesulfinate in acetonitrile good first-order kinetics were not observed. There is a downward drift apparent in the calculated first-order rate constants. The rate constants quoted are reproducible within experimental error. The addition of 0.11 M tetrabutylammonium 2-methylbenzenesulfinate resulted in ca. an 8% depression of the first-order rate constants. The amount of trityl azide produced under these conditions is $28.0 \pm 1.0\%$ (runs 3-226, 3-236 and 3-240).

The addition of ca. 0.2 M tetrabutylammonium 2-methylbenzenesulfinate caused ca. a 17% depression in the first-order rate constants. The amount of trityl azide produced is 18% (Table XV, runs 3-262 and 3-264). A sample rate calculation representing run 3-236 is shown in Table XVII. Figure XIV, shows a plot of $\log (C_{\infty} - C)$ against time.

When trityl 2-methylbenzenesulfinate is allowed to react with tetrabutylammonium azide and 2,6-dimethylbenzenesulfinate in acetonitrile, a steady downward drift is observed in the calculated first-order rate constants. The drift observed under these conditions is much more marked than when the ester is allowed to react with tetrabutylammonium azide in the presence of tetrabutylammonium perchlorate and 2-methylbenzenesulfinate salts. Runs 3-222, 3-230, 3-242 and 3-258 of Table XV, represent a summary of the results of the reaction of trityl 2-methylbenzenesulfinate with tetrabutylammonium azide and 2,6-dimethylbenzenesulfinate salts in acetonitrile. Tables XVIII, and XIX present sample rate calculations for runs 3-230

TABLE XVII

RATE OF REACTION OF TRITYL 2-METHYLBENZENESULFINATE (0.02017 M) WITH TETRA-BUTYLAMMONIUM AZIDE (0.06409 M) AND TETRABUTYLAMMONIUM 2-METHYLBENZENE-SULFINATE (0.10997 M) IN ACETONITRILE AT $25.23 \pm .24^{\circ}$ AT 2100 cm.⁻¹ RUN 3-236

Time (sec.)	Log I ₀ /I	Cobs mg/ml	k _{ob} x 10 ⁴ sec ⁻¹
0	0.0474	0.26	-
97	.0660	.36	8.02
241	.0884	.49	8.00
279	.0988	.55	8.92
376	.1154	.63	8.80
444	.1222	.68	8.70
565	.1381	.78	8.95
821	.1548	.90	8.15
851	.1663	.95	8.80
1020	.1741	1.01	8.35
1200	.1921	1.10	8.53
1702	.2122	1.22	(7.75)
2091	.2235	1.30	(7.55)
2435	.2353	1.38	8.88
3213	.2493	1.45	(7.47)
4703	.2592	1.50	(6.71)
6138	.2687	1.56	Avg = 8.57 ± .30
10331	.2684	1.56	
10212	.2740	1.58	
26616	.2744	1.58	

a - Rate constants indicated in brackets were omitted in calculating this average.. C_∞ = 1.57 mg/ml trityl azide = 27.3% of theoretical.

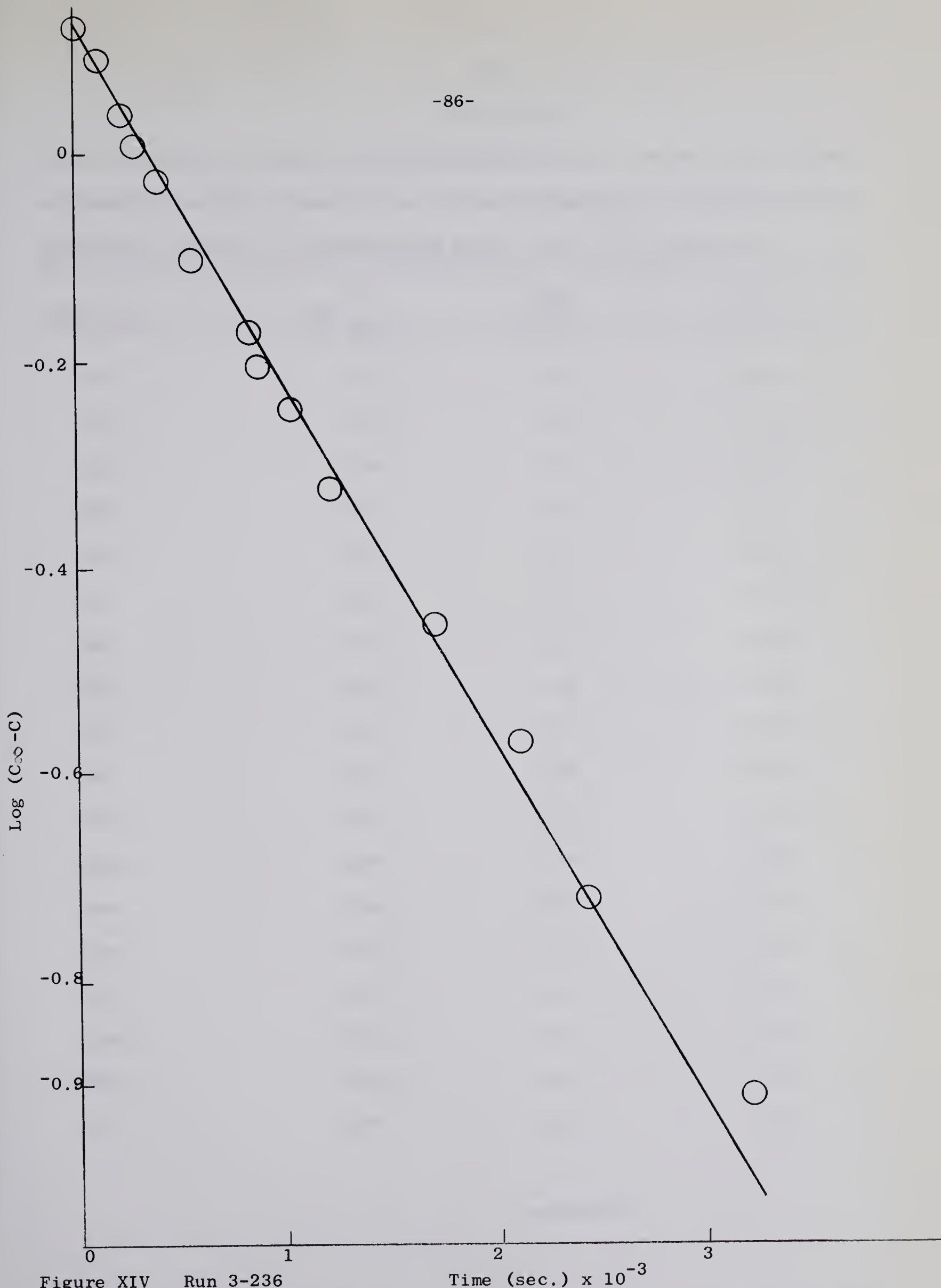


Figure XIV Run 3-236

Time (sec.) $\times 10^{-3}$

Relationship between $\log (C_{\infty} - C)$ against time for trityl 2-methylbenzenesulfinate with azide and 2-methylbenzenesulfinate salts in acetonitrile.

TABLE XVIII

RATE OF REACTION OF TRITYL 2-METHYLBENZENESULFINATE (0.02000 M) WITH TETRA-BUTYLAMMONIUM AZIDE (0.06409 M) AND TETRABUTYLAMMONIUM 2,6-DIMETHYLBENZENE-SULFINATE (0.10742 M) IN ACETONITRILE AT 25 .23 \pm .24^o RUN 3-230.

Time (sec.)	Log I_0/I	C _{obs} mg/ml	k x 10 ⁴ sec. ⁻¹
0	0.0693	0.38	-
87	.0972	.53	9.34
170	.1148	.62	7.86
259	.1320	.74	8.30
346	.1537	.90	9.13
432	.1743	1.03	9.56
521	.1825	1.05	8.26
605	.1972	1.15	8.50
683	.2047	1.18	7.90
761	.2144	1.24	7.78
843	.2207	1.30	7.73
1034	.2322	1.35	6.70
1258	.2649	1.53	7.25
1469	.2834	1.62	7.15
1689	.2949	1.73	7.18
1936	.3036	1.76	6.50
2305	.3110	1.80	5.82
2689	.3168	1.85	5.40
3135	.3271	1.92	5.15

contiuned

TABLE XVIII (continued)

4463	.3448	2.01	4.12
5455	.3492	2.05	3.73
5605	.3539	2.09	3.94
7273	.3663	2.16	3.60
8416	.3652	2.16	3.10
9230	.3722	2.21	3.32
11220	.3813	2.29	
22200	.3912	2.35	
36000	.3839	2.30	
87420	.3828	2.30	

$C_{\infty} = 2.30 \text{ mg/ml} \quad \bar{=}$ 40.4% trityl azide of theoretical.

k - from initial slope. $8.67 \times 10^{-4} \text{ sec.}$
 k - from final slope. $2.26 \times 10^{-4} \text{ sec.}$

} From Figure XV

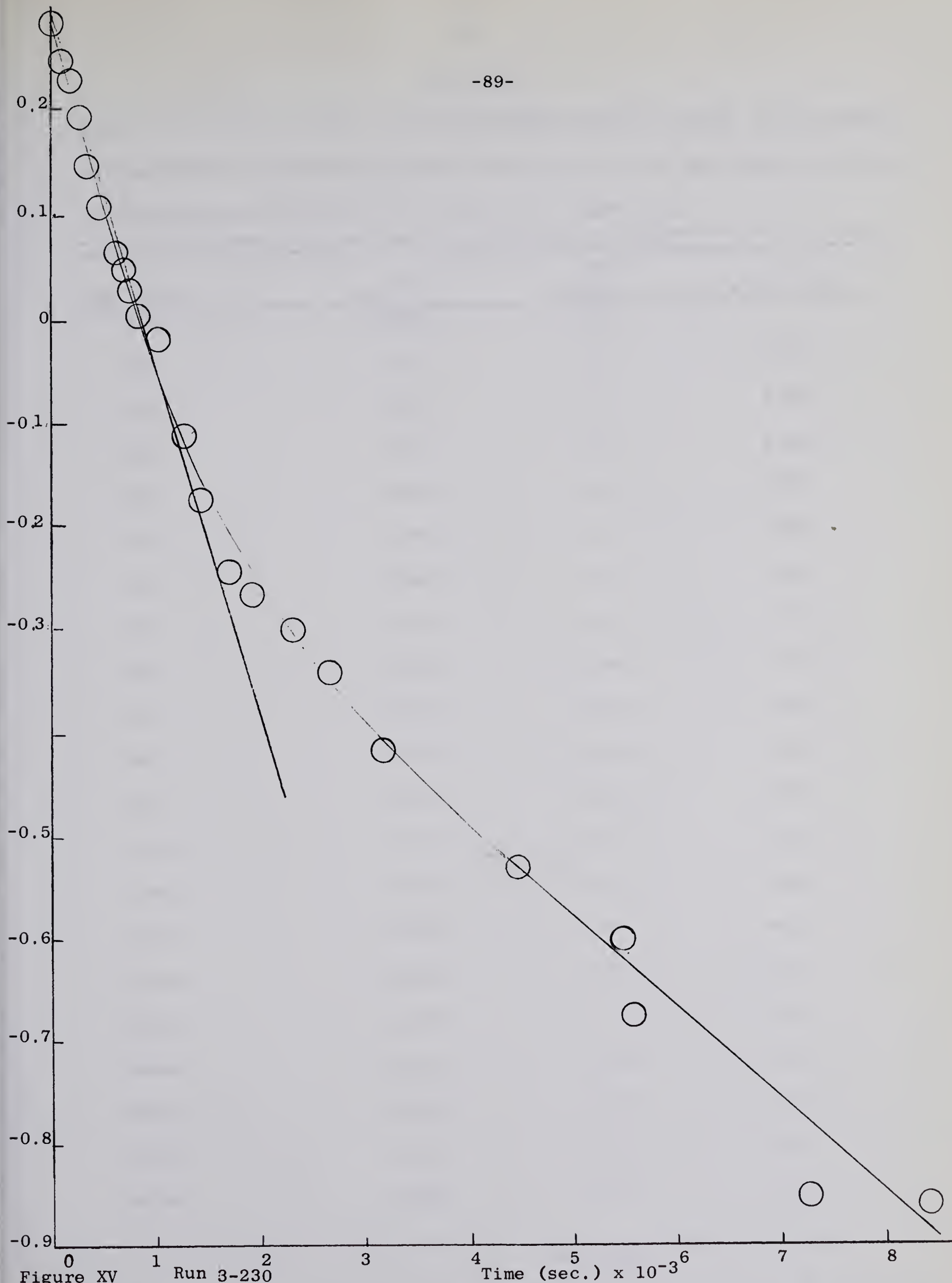


Figure XV Run 3-230

Relationship between $\log (C_\infty - C)$ and time for the reaction of trityl 2-methylbenzenesulfinate with azide and 2,6-dimethylbenzenesulfinate ions in acetonitrile.

TABLE XIX

RATE OF REACTION OF TRITYL 2-METHYLBENZENESULFINATE (0.02068 M) WITH TETRA-BUTYLAMMONIUM 2,6-DIMETHYLBENZENESULFINATE (0.23172 M) AND AZIDE (0.06715 M) IN ACETONITRILE AT 2100 cm^{-1} AT $25.23 \pm .24^\circ$. RUN 3-242

Time (sec.)	$\text{Log } I_0/I$	C_{obs} mg/ml	$k \times 10^4 \text{ sec.}^{-1}$
0	0.0961	0.51	-
88	.1121	.61	.6.20
171	.1337	.75	6.64
255	.1491	.86	8.05
333	.1655	.96	8.20
411	.1779	1.03	7.85
484	.1896	1.09	7.60
557	.2014	1.16	7.60
631	.2135	1.24	7.75
722	.2254	1.30	7.90
792	.2321	1.35	7.65
948	.2475	1.44	7.30
1141	.2664	1.55	7.15
1332	.2836	1.64	6.99
1694	.2958	1.73	6.25
2118	.3069	1.79	5.40
2533	.3249	1.89	5.24
2893	.3261	1.96	5.10
3923	.3428	2.00	4.00
5114	.3615	2.13	3.50
6197	.3633	2.15	3.32

continued

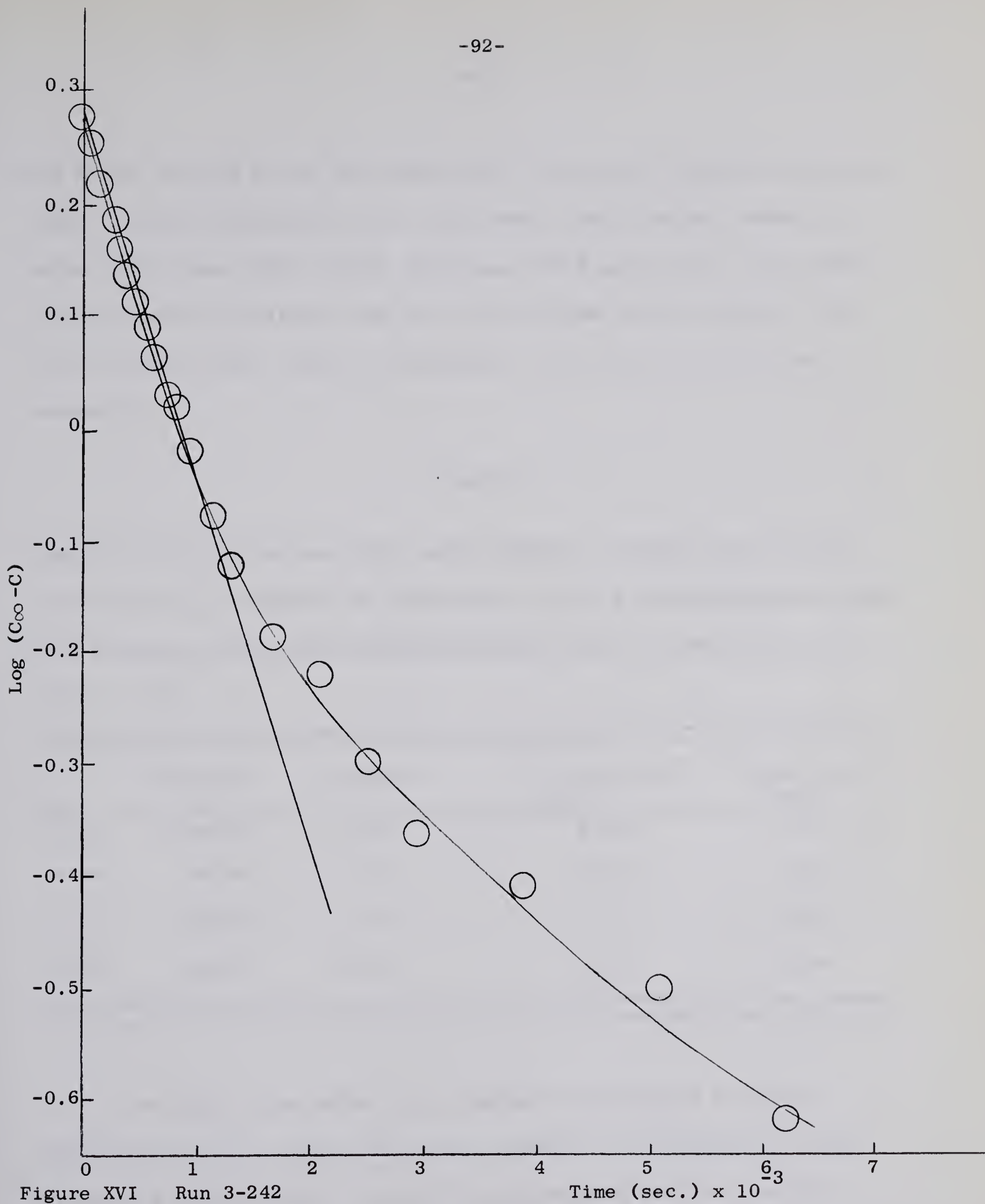
TABLE XIX (contiuned)

7272	.3762	2.25	3.54
			3.17
8654	.3783	2.27	
15600	.3780	2.26	
88200	.3916	2.36	
108000	.3971	2.39	
129600	.3964	2.38	
180000	.4052	2.40	

$C_{\infty} = 2.39 \text{ mg/ml} \equiv 40.5\% \text{ trityl azide of theoretical.}$

$k - \text{from initial slope } 7.50 \times 10^{-4} \text{ sec.}^{-1}$

$k - \text{from final slope } 2.08 \times 10^{-4} \text{ sec.}^{-1}$



Relationship between $\log (C_{\infty} - C)$ and time for the reaction of trityl 2-methylbenzenesulfinate with azide and 2,6-dimethylbenzenesulfinate ions in acetonitrile.

and 3-242. Figures XV and XVI show plots of $\log (C_{\infty}-C)$ against time for these two runs respectively. The first-order rate constants shown in Table XV for runs 3-222, 3-230, 3-242 and 3-258 are initial first-order rate constants calculated from the initial slopes of the plots of $\log (C_{\infty}-C)$ against time. Table XX summarizes the initial and final rate constants.

TABLE XX

SUMMARY OF THE INITIAL AND FINAL RATE CONSTANTS OBTAINED FROM PLOTS OF $\log (C_{\infty}-C)$ v.s. TIME FOR THE REACTION OF TRITYL 2-METHYLBENZENESULFINATE WITH AZIDE AND 2,6-DIMETHYLBENZENESULFINATE SALTS IN ACETONITRILE AT $25.23 \pm 0.24^{\circ}$.

Run	Sulfinate M	(2,6-salt) M	$k_{\text{initial}} \times 10^4$ sec^{-1}	$k_{\text{final}} \times 10^4$ sec^{-1}
3-222	0.02098	0.10870	8.58	1.08
3-230	.02000	.10742	8.67	2.26
3-242	.02068	.23172	7.50	2.08
3-258	.02073	.23124	7.80	2.44

The final first-order rate constants are subject to large experimental errors, since the points involved in obtaining the final slopes were usually after the reaction had reached greater than 80% completion. In run 3-222 only 4 points were taken after 80% reaction and less accuracy is associated with k_{final} here as compared to its

duplicate 3-230 where 9 points were taken after 80% reaction. The addition of tetrabutylammonium 2,6-dimethylbenzenesulfinate had no effect on the amount of trityl azide formed in the reaction. Under these conditions $41 \pm 1.0\%$ trityl azide is produced. (Runs 3-222, 3-230, 3-242 and 3-258 of Table XV).

When trityl 2-methylbenzenesulfinate was allowed to react with tetrabutylammonium azide and perchlorate in acetonitrile good first-order kinetics were not observed. The first-order rate constants drifted steadily downward after about 84% reaction. The addition of tetrabutylammonium perchlorate has no effect on the amount of trityl azide produced. Table XXI shows a summary of the results obtained. A sample rate representing run 3-254 is shown in Table XXII. Figure XVII shows a plot of $\log (C_{\infty} - C)$ against time.

TABLE XXI

THE REARRANGEMENT AND SUBSTITUTION OF TRITYL 2-METHYLBENZENESULFINATE WITH TETRABUTYLAMMONIUM AZIDE AND PERCHLORATE SALTS IN ACETONITRILE AT $25.23 \pm .24^{\circ}$, AT 2100 cm^{-1}

Run	(Ester) M	(N_3^-) M	(ClO_4^-) M	$k_1 \times 10^4$ sec^{-1}	F _{azide}
3-252	0.01874	0.06364	0.1000M	8.54 ^a	0.41
3-254	.02484	.06364	.2024M	7.92 ^a	.41

a - These values are calculated from plots of $\log (C_{\infty} - C)$ against time using the initial slopes.

TABLE XXII

RATE OF REACTION OF TRITYL 2-METHYLBENZENESULFINATE (0.02484 M) WITH TETRA-BUTYLAMMONIUM AZIDE (0.06364 M) AND PERCHLORATE (0.2024 M) IN ACETONITRILE AT 2100 cm^{-1} , AT $25.23 \pm .24^{\circ}$. RUN 3-254

Time (sec.)	Log I_0/I	C_{ob} mg/ml	$k_1 \times 10^4\text{ sec.}^{-1}$
0	0.10312	0.55	-
255	.18209	1.05	9.45
328	.19299	1.11	8.39
406	.21330	1.23	8.50
535	.22776	1.32	7.50
545	.24423	1.41	8.45
609	.25548	1.48	8.36
676	.26998	1.58	8.61
744	.27738	1.62	8.27
928	.30156	1.75	7.80
1069	.31555	1.83	7.45
1216	.32610	1.90	7.15
1515	.35645	2.10	7.24
2016	.38588	2.31	7.00
2288	.41142	2.49	7.84
2817	.41820	2.53	6.72
3557	.43442	2.65	6.49
4696	.44790	2.75	6.14
6031	.45026	2.77	5.06
7408	.46091	2.85	$k_{slope} = 7.92 \times 10^{-4}\text{ sec.}^{-1}$
14214	.47083	2.90	
29059	.47184	2.91	
102198	.46261	2.87	

$C_{\infty} = 2.88\text{ mg/ml trityl azide} \equiv 41\%$ of theoretical.

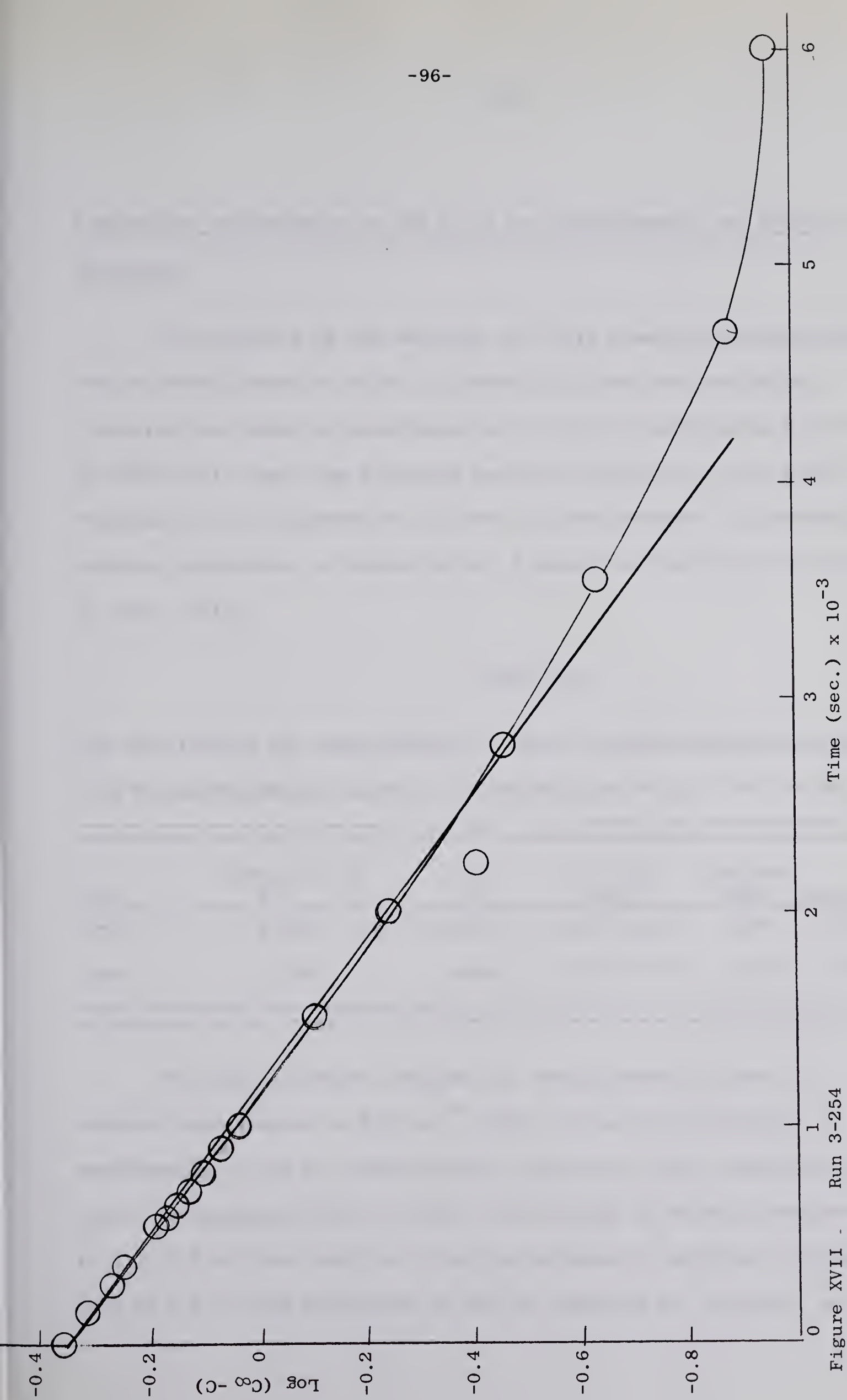


Figure XVII . Run 3-254

Relationship between $\log(C_{\infty} - C)$ and time for the reaction of trityl 2-methylbenzenesulfonate with tetrabutylammonium azide and perchlorate in acetonitrile.

Ultraviolet measurements at 283 mu of the Rearrangement and Substitution Processes.

The kinetics of the reaction of trityl 2-methylbenzenesulfinate with tetrabutylammonium azide in acetonitrile was also studied by following the change in absorbance due to trityl 2-methylphenyl sulfone at 283 mu with time. The procedure used was identical to that used for studying the rearrangement of the ester in the presence of tetrabutylammonium perchlorate in acetonitrile. A summary of the results is shown in Table XXIII.

TABLE XXIII

THE SUBSTITUTION AND REARRANGEMENT OF TRITYL 2-METHYLBENZENESULFINATE WITH TETRABUTYLAMMONIUM AZIDE IN ACETONITRILE AT $25.15 \pm .15^{\circ}$ AT 283 mu.

Run	(Ester) $\times 10^4$ M	(N_3^-) M	$k_1 \times 10^4$ sec^{-1}	F_{sulfone}	
				Obs.	Corrected.
4-22	9.033	0.07988	8.71 ± 0.20	0.67	54
4-8	9.109	.08324	8.70 ± 0.40	0.69	52

The rate constants obtained for disappearance of ester by infrared measurements at 2100 cm^{-1} (Table XV) and by ultraviolet measurements at 283 mu (Table XXIII) are identical within experimental error. In Table XXIII it is seen that the fraction of sulfone obtained is 0.68 ± 0.01 . The fraction of sulfone obtained by infrared analysis is 0.58 ± 0.20 . The absorbance at 283 mu, observed at "infinity" is

due to trityl 2-methylphenyl sulfone, trityl azide, and tetrabutylammonium 2-methylbenzenesulfinate. The latter two compounds have small but observable absorbances at this wavelength. The absorbance due to trityl azide ($\epsilon = 159$) and tetrabutylammonium 2-methylbenzenesulfinate ($\epsilon = 180$) at 283 μ were determined. The sum of these absorbances were subtracted from the absorbance observed at the end of the reaction to give the absorbance due to trityl 2-methylphenyl sulfone. From the plot of absorbance against concentration a corrected value for the fraction of sulfone produced in the reaction was determined. This value is 0.53 ± 0.01 .

Product Analysis

Accurately weighed amounts of trityl 2-methylbenzenesulfinate tetrabutylammonium azide and 2,6-dimethylbenzenesulfinate were allowed to react in acetonitrile. At various times aliquots of this solution were worked up. After isolation the product mixture was dissolved in carbon disulfide and this solution was subjected to infrared and n.m.r. analyses. By comparing the integrated intensities of the n.m.r. signal at $\tau 7.6$ due to the 6 methyl protons of trityl 2,6-dimethylbenzenesulfinate, to the signal at $\tau 8.3$ due to the 3 methyl protons of trityl 2-methylphenyl sulfone the amount of ester relative to sulfone was determined. The results of the product analyses are shown in Table XXIV.

It is seen that 4 minutes after mixing the reactants, 2.1% of trityl 2,6-dimethylbenzenesulfinate relative to trityl 2-methylphenyl sulfone is formed. After 25 minutes 4.01% ester relative to sulfone is produced. After 120 minutes when all trityl 2-methylbenzenesulfinate

TABLE XXIV

PRODUCT ANALYSIS OF THE REACTION OF TRITYL 2-METHYLBENZENESULFINATE WITH TETRABUTYL-AMMONIUM AZIDE AND 2,6-DIMETHYLBENZENESULFINATE IN ACETONITRILE AT 25.00 \pm .01.

Run	(2-ester) M	(N ₃) M	(2,6-salt) M	Time (min.)	Estimated % reaction of 2-ester	Relative intensities and J values of methyl protons				% 2,6-ester relative to sulfone
						2-ester J 7.8	(a) Sulfone J 8.28	(b) 2,6-ester J 7.6	(c)	
3-222	0.02098	0.06409	0.10870	120	100	-	5.6	1.1		9.8
4-10A	.01037	.05732	.10766	4	30	57	12	0.5		2.1
4-10B	"	"	"	25	74	5.0	14	1.1		4.0
4-10C	"	"	"	120	100	-	51	11.0		10.8

(a) - Trityl 2-methylbenzenesulfinate.

(b) - Trityl 2-methylphenyl sulfone.

(c) - Trityl 2,6-dimethylbenzenesulfinate.

has disappeared $10.3 \pm 0.5\%$ of trityl 2,6-dimethylbenzenesulfinate relative to trityl 2-methylphenyl sulfone is produced.

Product run 3-222 of Table XXIV was carried out in conjunction with kinetic measurements, (c.f. run 3-222, Table XV), therefore it is possible to estimate the extent of reaction of trityl 2-methylbenzenesulfinate at various times under the conditions of the product study. For run 3-222 a Varian Analytical Spectrophotometer Model A-60 was used, however to obtain better accuracy a Varian Analytical Spectrophotometer Model HR-100 was used for subsequent runs (runs 4-10A, 4-10B and 4-10C). The results show good agreement, (Compare runs 3-222 and 4-10C of Table XXIV).

Competition experiments with azide and 2-methylbenzenesulfinate ions.

Trityl perchlorate was allowed to react with tetrabutylammonium azide and 2,6-dimethylbenzenesulfinate in acetonitrile at 25° . Immediately after mixing and at appropriate times thereafter the solution was subjected to quantitative infrared analysis to determine the amount of trityl azide and trityl 2,6-dimethylbenzenesulfinate formed.

The amount of trityl azide formed initially was estimated from the absorbance values at 2100 cm^{-1} . The amount of trityl 2,6-dimethylbenzenesulfinate formed in the reaction was conveniently determined by allowing the ester produced to react to completion with tetrabutylammonium azide. The time chosen is more than 10 half-lives for the disappearance of trityl 2,6-dimethylbenzenesulfinate under analogous conditions, estimated

from the first-order rate constants for the disappearance of ester reported in Chapter III. By comparing the amount of trityl azide produced initially to the amount produced at infinity, both the amount of trityl azide and trityl 2,6-dimethylbenzenesulfinate produced on mixing may be determined. The results of the competition reactions are given in Table XXV.

TABLE XXV

THE REACTION OF TRITYL PERCHLORATE WITH TETRABUTYLAMMONIUM AZIDE AND 2,6-DIMETHYLBENZENESULFINATE IN ACETONITRILE AT $25.00 \pm 0.01^{\circ}$.

Run	(N ₃ ⁻) M	(2,6-salt) M	Time (hrs)	Log I ₀ /I	Cob mg/ml	%RN ₃	%2,6-ester
4-70	0.0607M	0.05994	0	0.4236	2.58	90.3	9.7
			2.4 hr.	.4468	2.73	95.4	4.6
			33.5 hr.	.4682	2.86	100%	-
			71.5 hr.	.4675	2.86	100%	-
4-72	0.06442	0.1923	0	.3644	2.15	78%	22.0
			59.7 hr.	.4506	2.76	100%	-

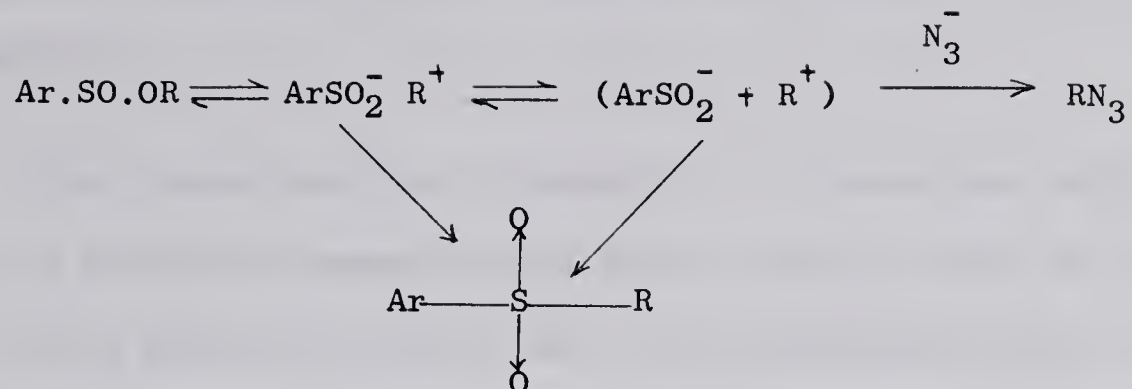
DISCUSSION

Darwish and Preston (56) previously suggested that the rearrangement and substitution reactions of trityl 2-methylbenzenesulfinate with tetrabutylammonium azide in acetonitrile are both ionic in nature. It was further suggested that some, but not all of the rearrangement occurred via an easily capturable carbonium ion intermediate. It is conceivable that the portion of the rearrangement which cannot be intercepted by azide ion could occur by a concerted, cyclic, non-polar reaction. A concerted cyclic rearrangement of allylic arenesulfonates to sulfones via a five membered ring transition state has been observed to occur (61). However in non-allylic systems where a three membered ring transition state is required for this mode of rearrangement, there does not appear to be any evidence for the rearrangement occurring in this manner.

In Chapter I it was shown that the rearrangement reaction of the ester in chloroform involved an ionic intermediate. Acetonitrile is a better ionizing solvent than chloroform (55). Therefore it follows that the rearrangement of trityl 2-methylbenzenesulfinate to trityl 2-methylphenyl sulfone in acetonitrile must also involve ionic intermediates.

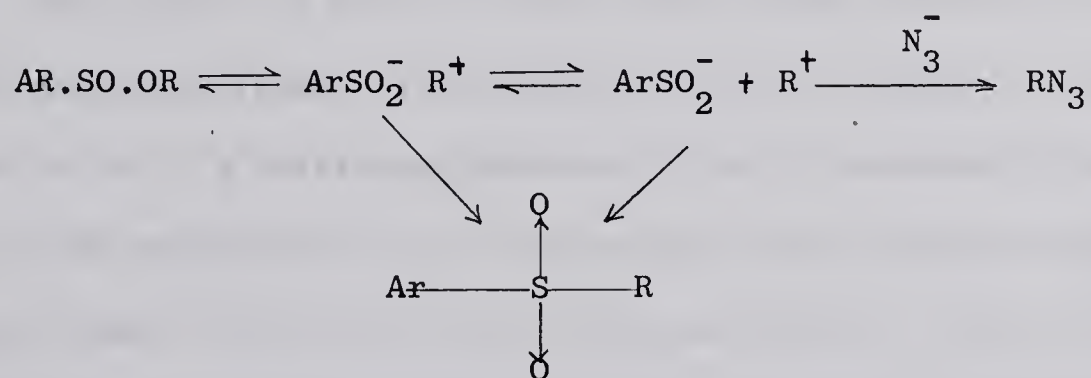
It is felt that the following scheme first suggested by Darwish and Preston (56) is consistent with the observed facts.

SCHEME I



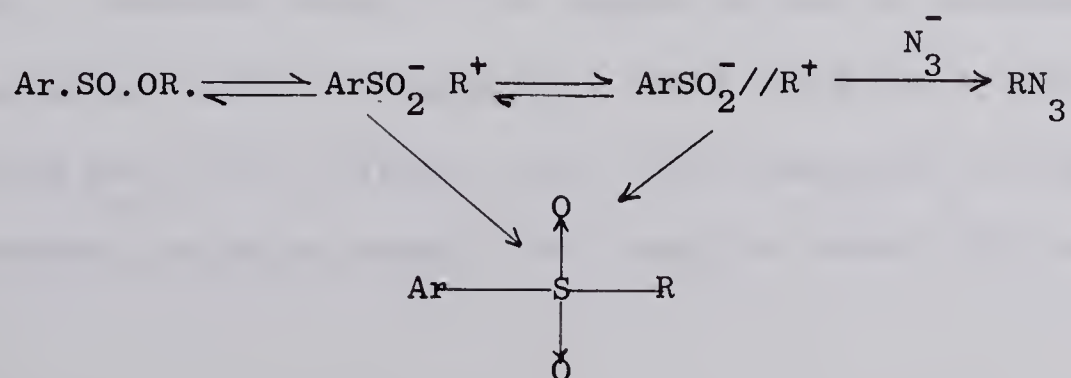
In this scheme $(\text{ArSO}_2^- + \text{R}^+)$ is the capturable intermediate and may be equated with the solvent separated ion pair or free ions or both. It remains to attempt to ascertain the nature of the species which is captured under the conditions of this study. Let us consider the two possibilities,

SCHEME II



In this scheme the capturable species is depicted as a dissociated ion.

SCHEME III



In Scheme III the solvent separated ion pair, $\text{ArSO}_2^-//\text{R}^+$ is the trappable intermediate.

From a consideration of Scheme II it is seen that addition of the common ion 2-methylbenzenesulfinate should result in more of the free trityl cation being captured by the 2-methylbenzenesulfinate ions, leading to a decrease in trityl azide yield and a decrease in the rate of disappearance of the ester.

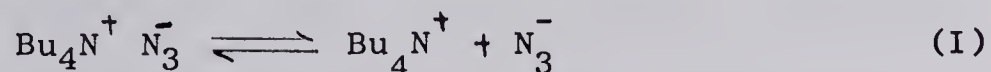
If however the reaction were proceeding by a pathway as depicted by Scheme III, then addition of the common ion should to a first approximation have no effect on the yield of trityl azide, and also no effect on the rate of disappearance of the ester.

The results of Table XV show that in the reaction of trityl 2-methylbenzenesulfinate with tetrabutylammonium azide in acetonitrile addition of 0.11 M tetrabutylammonium 2-methylbenzenesulfinate resulted in ca. an 8% depression of the first-order rate constant (Compare runs 3-214 and 3-224 with runs 3-226, 3-236 and 3-240 of Table XV.) The addition of ca. 0.2 M 2-methylbenzenesulfinate salt caused about a 15% depression in rate, (Compare runs 3-214 and 3-244 with runs 3-262 and 3-264 of Table XV). However an almost identical depression of the rate constant is observed when similar concentrations of tetrabutylammonium perchlorate are added, (Compare runs 3-214 and 3-224 of Table XV with runs 3-252 and 3-254 of Table XXI). This depression of the first-order rate constant may be an example of a mass law effect (32) but if so,

cannot be associated with the 2-methylbenzenesulfinate ion. One might consider a depression in rate due to the tetrabutylammonium ion as outlined below.

It has been shown that trityl 2-methylbenzenesulfinate rearranges to trityl 2-methylphenyl sulfone in acetonitrile in the absence of added salts, and that the rate of disappearance of the ester in the presence of tetrabutylammonium azide is ca. twice as fast as in the absence of this salt. (Compare the results of runs 3-279 and 3-282 of Table XI with runs 3-214 and 3-224 of Table XV.) This difference in rate is due to the fact that azide ion intercepts a portion of the trityl cations which would normally regenerate the starting ester, and diverts them to trityl azide. Preston (55) has shown that in the reaction of the ester with tetrabutylammonium azide in acetonitrile the yield of trityl azide increases with increasing azide salt concentration in the range of concentrations up to ca. 0.05 M salt. When the concentration of tetrabutylammonium azide is above 0.05 M the trityl azide yield is independent of the concentration of azide salt.

Tetrabutylammonium azide must exist partly as dissociated entities and partly in the form of ion pairs (higher aggregates will be neglected) as shown in Equation I.



It seems reasonable to assume that the free azide ion would be more effective than the salt ion pair at capturing the trityl cation,

and to a first approximation may be considered the only effective trapping agent. If this assumption were correct, then above a tetrabutylammonium azide concentration of ca. 0.05 M there is a sufficient concentration of free azide ion to easily divert all of the capturable trityl cation to trityl azide and thus prevent its return to sulfone or starting ester.

The tetrabutylammonium azide concentration normally used in this study was ca. 0.064 M, which is above the required lower limit for complete capture. However when other tetrabutylammonium salts are added the equilibrium in Equation I will be shifted in such a way that some of the free azide ions will be converted to the ion pair form. If the concentration of free azide ion were reduced below the required minimum value, capture of the trityl cation will no longer be 100% efficient. This will result in some of the trityl cation returning to starting ester causing a reduction in the rate of disappearance of ester. This should also result in a decrease in the yield of trityl azide. To a first approximation this reduction in rate and trityl azide yield should be essentially independent of the nature of the negative ion.

The phenomenon observed when either tetrabutylammonium 2-methylbenzenesulfinate or perchlorate is added to the solution is an identical reduction in the rate of disappearance of the ester due to these two salts. However the yield to trityl azide is unaffected on addition of tetrabutylammonium perchlorate, while the presence of the 2-methylbenzenesulfinate salt resulted in a reduction in the yield of trityl azide depending on the concentration of tetrabutylammonium 2-methylbenzene-

sulfinate employed. Therefore this simple explanation is not consistent with all the results. This may mean that the depression in rate observed may not reflect any form of common ion rate depression.

The kinetic results are consistent with Scheme II, if common ion rate depression is small. The increased yield of sulfone observed on addition of the 2-methylbenzenesulfinate salt is consistent with a mechanism that involves dissociated ions as shown in Scheme II. However one can rationalize this exchange reaction as proceeding via Scheme III, but must visualize a back reaction between a trityl azide ion pair with 2-methylbenzenesulfinate to regenerate the trityl 2-methylbenzenesulfinate ion pair, following which collapse of this species will give starting ester or sulfone. It seems unlikely that this back reaction will take place due to the powerful nucleophilicity associated with the azide ion (63).

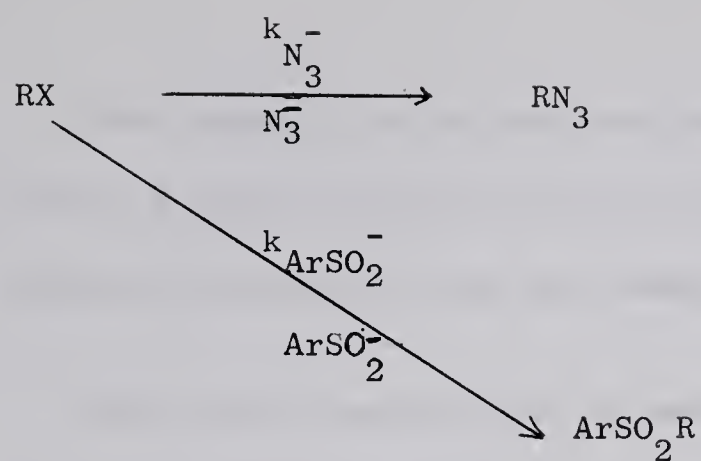
From the above discussion it is seen that it is not possible to make a definite decision as to the nature of the species which is captured under the present conditions.

Competition Factors

One other consideration of the salt effects involves the competition reactions. The competition factors may be calculated from the formula

$$\frac{k_{N_3^-}}{k_{ArSO_2^-}} = \frac{F_{RN_3} (ArSO_2^-)}{F_{ArSO_2} R (N_3^-)}$$

which may be derived in the following way.



$$\frac{d(\text{RN}_3)}{dt} = k_{\text{N}_3^-} (\text{N}_3^-) (\text{RX})$$

$$\frac{d(\text{ArSO}_2\text{R})}{dt} = k_{\text{ArSO}_2^-} (\text{ArSO}_2^-) (\text{RX})$$

$$\frac{(\text{RN}_3)}{(\text{ArSO}_2\text{R})} = \frac{k_{\text{N}_3^-} (\text{N}_3^-)}{k_{\text{ArSO}_2^-} (\text{ArSO}_2^-)}$$

$$\text{Let } F_{\text{RN}_3} = \frac{(\text{RN}_3)}{(\text{RN}_3) + (\text{ArSO}_2\text{R})}$$

$$\text{and } F_{\text{ArSO}_2\text{R}} = \frac{(\text{ArSO}_2\text{R})}{(\text{ArSO}_2\text{R}) + (\text{RN}_3)}$$

$$\text{Then } \frac{k_{\text{N}_3^-}}{k_{\text{ArSO}_2^-}} = \frac{F_{\text{RN}_3} (\text{ArSO}_2^-)}{F_{\text{ArSO}_2\text{R}} (\text{N}_3^-)}$$

The competition factors obtained in the reaction of trityl perchlorate and trityl 2-methylbenzenesulfinate with tetrabutylammonium azide and 2,6-dimethylbenzenesulfinate are summarized in Table XXVI.

When trityl perchlorate is used as substrate the calculations are based on the fraction of products which are formed immediately upon mixing the reactions. For example, the azide/2-methylbenzenesulfinate competition factor was calculated based on the value of $F_{\text{ArSO}_2\text{R}} = 0.55$, which is the sum of the fractions of trityl 2-methylbenzenesulfinate and trityl 2-methylphenyl sulfone produced in the reaction. When trityl 2-methylbenzenesulfinate is employed as the substrate the competition factors were estimated in the following manner.

If run 3-222 is used as an example it is seen that in the reaction of trityl 2-methylbenzenesulfinate with tetrabutylammonium azide in the presence of 0.11 M tetrabutylammonium 2,6-dimethylbenzenesulfinate resulted in the formation of 9.8% of trityl 2,6-dimethylbenzenesulfinate relative to trityl 2-methylphenyl sulfone after two hours (Table XXIV). Two hours is approximately 10 half-lives for the disappearance of trityl 2-methylbenzenesulfinate. After this time the reaction yields 58% of trityl 2-methylphenyl sulfone. Therefore 5.9% of trityl 2,6-dimethylbenzenesulfinate is formed in the reaction. In the absence of the 2,6-dimethylbenzenesulfinate salt a 42% yield of trityl azide is obtained. Therefore in the presence of this salt a 36.1% (42 - 5.9) yield of trityl azide is obtained from the capturable carbonium ion. From the values, $F_{\text{RN}_3} = 0.361$ and $F_{\text{ArSO}_2\text{R}} = 0.059$, together with the appropriate concentrations

TABLE XXVI

COMPETITION FACTORS OBTAINED IN THE REACTIONS OF TRITYL PERCHLORATE AND TRITYL
2-METHYLBENZENESULFINATE WITH TETRABUTYLAMMONIUM AZIDE, 2-METHYLBENZENESULFINATE
AND 2,6-DIMETHYLBENZENESULFINATE IN ACETONITRILE AT 25°.

Run	Substrate	(\bar{N}_3) M	(2-Salt) M	(2,6-salt) M	F_{RN_3}	F_{ArSO_2R}	$k_{N_3^-}/k_{ArSO_2^-}$
4-70	Trityl perchlorate	0.06070	-	0.05994	0.90	0.097	9.3
4-72	"	.06442	-	.1923	.78	.22	10.6
-(b)	"	.071	0.071	-	.45	.55	.82 ^(b)
3-222	Trityl 2-methylbenzene- sulfinate	.06409	-	.1087	.36	.059	10.9 ^(a)
4-10C	"	.05732	-	.10766	.37	.054	12.7 ^(a)

(a) - These numbers are not corrected for the fraction of trityl 2,6-dimethylbenzenesulfinate which yields trityl azide as the reaction progresses.

(b) - Results taken from reference (56).

listed in Table XXVI for run 3-222 the competition factor of 10.9 was obtained.

From considerations of the competition factors it is seen that the extra methyl group of the 2,6-dimethylbenzenesulfinate ion makes this nucleophile a relatively poor trap for the trityl cation, when compared to the 2-methylbenzenesulfinate and azide ions, which show about equivalent trapping ability.

EXPERIMENTAL

Acetonitrile;

Fisher certified reagent grade acetonitrile was purified according to the method described by Smith, Fainberg and Winstein (70). The solvent was first distilled from phosphorous pentoxide, then refluxed over anhydrous potassium carbonate for two hours, filtered, and then redistilled from phosphorous pentoxide. The center cut was used, b.p. 79° , n_D^{25} 1.3421 (reported (70), n_D^{25} 1.3420).

2,6-Dimethylbenzenesulfinic acid (58)

This compound was prepared in the same manner as described for the 2-methylbenzenesulfinic acid in Chapter I. Starting with 2,6-dimethylaniline (57 g., 0.46 mole), 68 g. (80%) of white crystalline acid was obtained, m.p. $92 - 93^{\circ}$ (with decomposition), reported (61) m.p. $92 - 94^{\circ}$.

2,6-Dimethylbenzenesulfinyl chloride (58)

This compound was prepared using the procedure described for 2-methylbenzenesulfinyl chloride. 2,6-Dimethylbenzenesulfinic acid (17 g., 0.089 mole), yielded 15 g., (80.0%) of a yellow oil.

Trityl 2,6-dimethylbenzenesulfinate (55)

A 15 g. quantity (0.08 mole) of 2,6-dimethylbenzenesulfinyl chloride was allowed to react with 10.4 g. (0.040 mole) triphenylcarbinol in 69 ml. pyridine, cooled in an ice-methanol bath maintained at -15° to -18° . After 25 minutes the flask was transferred to the freezing compartment of a refrigerator and left there for an additional

26 hours. The work-up procedure used was the same as outlined for the 2-methylbenzenesulfinate ester. Purification was effected by recrystallization from warm ether to give 10 g. of product m.p. $92 - 94^{\circ}$; reported (55) m.p. $92 - 93.5^{\circ}$

Infrared and n.m.r. spectra in carbon disulfide were compared to, and found to be identical with spectra of the authentic material kindly donated by Dr. D. Darwish. Infrared (CS_2) : 700, 770, 900, and 1135 cm^{-1} , n.m.r. (CS_2) : 2.5 - 3.5 (m) and $\tau 7.2$ (s), ratio 3.05 : 1 (calculated ratio 3 : 1.) Equivalent weight on hydrolysis found 408.5 , calculated 412.6 .

Analysis calculated for	$\text{C}_{27}\text{H}_{24}\text{SO}_2$:	C, 78.62	H, 5.86
	Found	:	C, 78.50	H, 5.89
			78.71	6.03

Trityl isothiocyanate:

This compound was kindly donated by E.A. Preston.

Trityl azide : (13, 55)

This compound was synthesized by a procedure suggested by Swain (13), with a few minor modifications. Fisher reagent grade sodium azide (8.15 g., 0.125 mole) was dissolved in 325 ml. water. This solution was added to a solution of 12.5 g. (0.042 mole) trityl isothiocyanate in 500 ml. of acetone. After 24 hours at room temperature, 625 ml. water was added and the solution extracted three times with ether and once with benzene. The combined extracts were dried over magnesium sulfate, filtered and the solvents removed by evaporation at the aspirator.

Three recrystallizations from ether-chloroform yielded 10 g. of brown crystals (83%) of trityl azide m.p. $62 - 64^{\circ}$, reported (13) m.p. $64.5 - 65.5^{\circ}$, (55) $62 - 64^{\circ}$. Infrared (carbon disulfide) 700, 750, 1250, and 2100 cm^{-1} .

Analysis calculated for	$\text{C}_{19}\text{H}_{15}\text{N}_3$:	C, 79.98	H, 5.30	N, 14.72
	Found	:	C, 79.91	H, 5.28	N, 14.78
			79.72	5.30	

Tetra-n-butylammonium salts :

The preparations of tetra-n-butylammonium bromide and tetra-n-butylammonium hydroxide have been described in Chapter I.

Tetra-n-butylammonium azide (71)

Tetra-n-butylammonium bromide (81 g., 0.25 mole) was used to prepare tetra-n-butylammonium hydroxide in water. Hydrazoic acid, prepared by adding 84 ml. concentrated sulfuric acid to 30 g., sodium azide contained in 75 ml. water and 75 ml. ether, was then distilled by heating on a steam bath, into the flask containing the hydroxide, which was maintained at -15 to -18° (ice-methanol). The hydrazoic acid was added until the reaction mixture showed a pH of 5. The pale yellow solution was concentrated to about 70 ml. at the aspirator and the resulting oil was extracted with chloroform. The chloroform solution of the salt was treated with decolorizing charcoal, and after filtration most of the chloroform was removed at the aspirator. The flask now containing an oily residue, was stored under vacuum in a dessicator containing phosphorous pentoxide until dry and solid. The white crystals

obtained were recrystallized three times from ethyl acetate-ether, to yield 60 g. (83%) of white hygroscopic crystals, which were stored in a vacuum dessicator containing phosphorous pentoxide. Infrared and n.m.r. spectra were superimposable upon those of an authentic sample kindly donated by Dr. D. Darwish.

Tetra-n-butylammonium perchlorate :

Tetra-n-butylammonium perchlorate crystallized as a white solid, when tetra-n-butylammonium hydroxide was neutralized with 70% perchloric acid. Thus 40 g. (0.12 mole) tetra-n-butylammonium bromide yielded 37 g. (80%), tetra-n-butylammonium perchlorate after three recrystallizations from ethyl acetate-pentane. M.p. 212.0 - 212.5^o., reported (25), 212.0 - 212.5^o.

Tetra-n-butylammonium 2-methylbenzenesulfinate (55)

Tetrabutylammonium bromide (20 g., 0.0621 mole) was dissolved in 30 ml. of water. Silver oxide was added to this solution and the mixture stirred, until a negative test for bromide ion was obtained. The solution was filtered. Solid 2-methylbenzenesulfinic acid was added to the filtrate, and the mixture stirred. Approximately 9 g. of acid were required to bring the solution to a desired pH of 8. The resulting slightly basic solution was concentrated at the aspirator and the yellow oil which resulted was stored under vacuum in a dessicator containing phosphorous pentoxide until dry and solid. The resulting yellow solid was recrystallized 4 times from ethyl-acetate-ether to give 15 g. (60%) of the desired product m.p. 105.8 - 106.8^o reported (56) m.p. 105 - 107^o. Infrared and n.m.r. spectra were superimposable

upon those of authentic spectra kindly supplied by Dr. D. Darwish.

Tetra-*n*-butylammonium 2,6-dimethylbenzenesulfinate :

This compound was prepared by the same method described for the 2-methylbenzenesulfinate salt. From tetra-*n*-butylammonium bromide (15 g., 0.047 mole), was obtained 12 g. (54%), white crystals of tetra-*n*-butylammonium 2,6-dimethylbenzenesulfinate. Infrared and n.m.r. spectra were identical to those of an authentic sample kindly supplied by Dr. D. Darwish.

KINETIC MEASUREMENTS

Ultraviolet :

A standard solution of 0.03 M 2,6-lutidine in purified acetonitrile was made up in a 500 ml. volumetric flask. In cases where salts were used a 250 ml. standard solution of the salt was prepared using the above 2,6-lutidine solution. The appropriate amount of trityl 2-methylbenzenesulfinate was accurately weighed into a 200 ml. volumetric flask and an aliquot of one of the above solutions, which was previously placed in a 25° thermostated water bath for 15 minutes, was added to the mark. The flask was thoroughly shaken, and a portion of the reaction solution transferred to a 1 cm., Beckman ultraviolet cell. Using a Beckman DU Spectrophotometer the absorption due to trityl 2-methylphenyl sulfone at 283 μ was determined. The time was recorded when the galvanometer needle reached equilibrium at the zero point. A blank reading was taken prior to every point.

Infrared :

A standard solution of tetra-n-butylammonium azide in acetonitrile was prepared in a 50 ml. volumetric flask. Trityl 2-methylbenzenesulfinate was accurately weighed into a 10 ml. volumetric flask and the azide solution added to the mark. If another salt was used together with azide, then this salt and ester were weighed into a 10 ml. volumetric flask, and azide solution added to the mark. The mixture was thoroughly shaken and a portion of the reaction solution transferred to a 0.5 mm. sodium chloride cell, which had been previously balanced against a variable spacer reference cell to compensate for any absorbance due to the solvent in the region to be scanned. Using a Perkin Elmer Model 21 Infrared Spectrophotometer with a 20 cm. per micron scale setting, the region $2200 - 2000 \text{ cm}^{-1}$ was scanned to determine the absorbance due to trityl azide at 2100 cm^{-1} . The time recorded for a particular point was that at which the percent transmittance reached a minimum.

Lambert-Beer Law Determinations

Trityl 2-methylphenyl sulfone in acetonitrile at 283 μ .

Trityl 2-methylphenyl sulfone ($125.4 \text{ mg.}, 6.293 \times 10^{-3} \text{ M}$) was weighed into a 50 ml. volumetric flask and acetonitrile added to the mark. Using a 5 ml. calibrated automatic pipette 5 ml. of this solution was transferred to a 50 ml. volumetric flask and acetonitrile added to the mark. Employing the same 5 ml. automatic pipette, 20 ml. of the latter solution was withdrawn and transferred to a 25 ml volumetric flask and acetonitrile added to the graduated mark. From this solution 5 ml. was transferred to

a 10 ml. volumetric flask with the aid of the same automatic pipette. Acetonitrile was added to the mark to obtain the desired concentration. A further dilution was made by withdrawing 5 ml. of solution from the last sample and transferring to a 10 ml. volumetric flask followed by addition of acetonitrile to the mark.

Using a Beckman DU Spectrophotometer these solutions were in turn analyzed at 283 μ . to determine the absorbance due to trityl 2-methylphenyl sulfone, by the same procedure used in the kinetic runs.

The above concentration range was later extended as can be seen in Table VII, by the same procedure described. The plot of absorbance against concentration is presented in Figure VII.

Trityl Azide in Acetonitrile at 2100 cm^{-1}

Trityl azide (184 mg.), was weighed into a 25 ml. volumetric flask and acetonitrile added to the mark. The mixture was shaken and with a calibrated automatic pipette 5 ml. of solution was withdrawn and transferred to a 10 ml. volumetric flask and acetonitrile added to the mark. From this solution and with the aid of the same pipette 5 ml. solution was transferred to a 10 ml. volumetric flask. Acetonitrile was added to the mark to give the described concentration. A further dilution was made by withdrawing 5 ml. from the latter solution and transferring to a 10 ml. volumetric flask and acetonitrile added to the mark.

These dilutions afforded solutions of 100, 50, 25, and 12½% trityl azide in acetonitrile. Further dilutions to obtain 75, 37.5 and 18.75% solutions were made. With the aid of the same 5 ml. automatic pipette 15 ml. of the original (100%) trityl azide solution was transferred to a 50 ml. Erlenmeyer flask, and with the same pipette, 5 ml. of acetonitrile was added. From this solution 37.5 and 18.75% solutions were made in the same manner as described for making 50 and 25% solutions respectively. Using a Perkin Elmer Model 21 Infrared Spectrophotometer the absorbance values at 2100 cm^{-1} , were determined in the manner described for the kinetic runs. TableXIV and FigureXII show the results of such determinations.

Product Isolation :

Trityl 2-methylbenzenesulfinate (2.115 g., 0.02123 M) was allowed to react in 250 ml. acetonitrile solution containing 0.06475 M tetrabutylammonium azide and 0.1056 M tetra-n-butylammonium 2,6-dimethylbenzenesulfinate. Two minutes after mixing a 100 ml. aliquot was withdrawn with an automatic pipette and poured into 100 ml. ether containing 2 ml. pyridine. The ether solution was washed six times with 100 ml. portions of water. The ether solution was then dried over magnesium sulfate, filtered and evaporated to dryness at the aspirator. Carbon disulfide was added, and a total infrared spectrum taken using a portion of this solution. Using a Varian Analytical Spectrophotometer Model HR-100 the remaining solution was subjected to n.m.r. spectroscopic analysis. The infrared spectrum had strong bands at 1135 and 1310 cm^{-1} , and a weak absorption at 2100 cm^{-1} . The above bands are consistent with the presence of sulfinate ester, trityl 2-methylphenyl sulfone and trityl

azide respectively. The n.m.r. spectra showed singlets at τ 7.6 τ 7.8 and τ 8.2. The signal at τ 7.6 is associated with the methyl protons of trityl 2,6-dimethylbenzenesulfinate. From the ratio of the integrated intensities of the o-methyl protons of trityl 2-methylphenyl sulfone at τ 8.28, to the methyl protons of trityl 2,6-dimethylbenzenesulfinate, it was found that 2% of trityl 2,6-dimethylbenzenesulfinate relative to trityl 2-methylphenyl sulfone was formed.

After 25 minutes another 100 ml. aliquot of the reaction mixture, (which was allowed to remain in a thermostated 25° water bath during the waiting period), was subjected to the same extraction procedure. The n.m.r. spectra showed singlets at τ 7.6, τ 7.8 and τ 8.2. From the ratio of the integrated intensities it was calculated that 4% of trityl 2,6-dimethylbenzenesulfinate relative to trityl 2-methylphenyl sulfone was formed.

The remaining 50 ml. of the reaction solution was worked up 120 minutes after mixing and subjected to the same treatment. The n.m.r. spectra revealed the presence of 10% trityl 2,6-dimethylbenzenesulfinate relative to trityl 2-methylphenyl sulfone.

Temperature Calibration (Infrared)

It was possible to maintain constant temperature when using the Perkin Elmer Model 21 Spectrophotometer for kinetic runs by the use of a Barnes Engineering Model 104 air tight cell compartment holder, equipped with a Barnes Engineering Model 102 Thermostat. By connecting a Biddle-Gray

T.C. Potentiometer which is calibrated in degrees Centigrade, it was possible at all times to tell the exact temperature of the air in the cell holder. The temperature of the reaction mixture was determined under conditions that were similar to an actual kinetic run. Trityl azide (0.0241 M) in acetonitrile was transferred to a sodium chloride cavity cell and a thermocouple lead made up of copper-constantan was placed into the cell. A tight fitting teflon stopper with a hollow bottom was used to hold the thermocouple lead in place. This design of stopper seemed to be best suited to prevent evaporation or seepage of the solvent up the wire of the lead. A 0° reference junction was used.

The cavity cell was then placed into the constant temperature cell thermostated at 25° . The Perkin Elmer Model 21 Infrared Spectrophotometer set at 4.79 microns (2100 cm^{-1}) the point of maximum absorption of the trityl azide band. The solution was then irradiated for one and a half minutes, and the light source was closed off for two minutes. Immediately as the light source was shut off the reading on a standard galvanometer was recorded. Eleven consecutive readings were taken over a period of 39 minutes. The results with the conversion to degrees centigrade is presented in Table LXXVII.

TABLE XXVII

TEMPERATURE CALIBRATION OF REACTION SOLUTION AT 2100 cm^{-1}

Number of consecutive readings	Millivolts	Temperature °C.
1	0.98	24.85
2	0.98	24.85
3	0.99	25.00
4	0.98	24.85
5	0.99	25.00
6	1.01	25.00
7	1.00	25.30
8	1.01	25.50
9	1.01	25.50
10	1.01	25.50
11	1.01	25.50
Average =		$25.23 \pm .30$

The change in temperature with time was also determined without the aid of the thermostated cell. The procedure used was identical to that described when the thermostated cell was employed. It was found that the temperature changed from 24.6° to 32° over a period of 25 minutes. The results of these determinations are given in Table XXVIII. It is probable that the difference between some of the rate constants reported here and those reported by Preston (55) is associated with the fact that Preston conducted his experiments without the aid of a thermostated cell.

TABLE XXVIII

TEMPERATURE CALIBRATION OF REACTION SOLUTION AT 2100 cm.^{-1} IN THE ABSENCE OF A THERMOSTATED CELL.

Number of consecutive readings	Millivolts	Temperature °C.
1	0.97	24.58
2	1.05	26.55
3	1.07	27.00
4	1.21	30.45
5	1.25	31.40
6	1.27	31.88
7	1.27	31.88
8	1.27	31.88
9	1.28	32.11
10	1.27	31.88

Temperature Calibration (Ultraviolet)

Trityl 2-methylphenyl sulfone (102.6 mg. 0.02574 M), was dissolved in a 10 ml. volumetric flask with acetonitrile. The Beckman DU Spectrophotometer thermostated at $25.10 \pm 0.02^{\circ}$ was set at 283 mu., the wavelength used for following the appearance of the sulfone band during kinetic determinations. A portion of the acetonitrile solution was transferred to a 1 cm. Beckman cell in which the thermocouple lead, was fitted. The cell was stoppered with a Telfon stopper and the readings recorded as before. The results are presented in Table XXIX.

TABLE XXIX

TEMPERATURE CALIBRATION OF REACTION SOLUTION AT 283 mu.

Number of consecutive readings.	Millivolts	Temperature °C.
1	1.00	25.30
2	1.00	25.30
3	0.99	25.00
4	1.00	25.30
5	1.00	25.30
6	0.99	25.00
7	0.99	25.00
8	1.00	25.30
9	0.99	25.00
10	1.00	25.30
11	0.99	25.00
Average =		25.15 ± .15°

After the above determinations were made the light source was opened continuously for half hour and one hour respectively. The temperature remained constant at 25.30°.

Competition Experiments;

A typical procedure will be given here using run 4-70 as an example.

Tetrabutylammonium azide (0.4317 g., 0.06070 M), and 2,6-dimethylbenzenesulfinate (0.6169 g., 0.05994 M), were weighed into a 25 ml. volumetric flask. Both salts were then brought into solution by the addition of ca. 20 ml. of purified acetonitrile. To this solution was added trityl perchlorate (0.0975 g., 0.0186 M) and the solution vigorously shaken to assist the dissolution of the salt. Acetonitrile was then added to the mark to give the required concentration.

A portion of the solution was transferred to a 0.5 mm matched sodium chloride cell, and the remainder of the solution stored at 25^o in a thermostated water bath. Using a Perkin Elmer Model 21 Infrared Spectrophotometer the region 2200 - 2000 cm.⁻¹, was scanned to determine the absorbance at 2100 cm.⁻¹, due to trityl azide in a manner that has been described previously. The time between mixing and taking the first reading was 2 minutes. From the absorbance value at 2100 cm.⁻¹, the concentration in mg/ml, of trityl azide formed initially was determined from the plot of absorbance against concentration.

In this particular example the amount of trityl azide produced over a period of time was determined by analyzing the solution at various times (See Table XXV). The percentage trityl azide was found to slowly increase with time, indicating that trityl 2,6-dimethylbenzenesulfinate was formed as one of the first products of the reaction. Analysis of the solution 33 and 72 hours after mixing showed no change in the amount of trityl azide produced.

The fraction of trityl 2,6-dimethylbenzenesulfinate produced initially in the reaction was determined by dividing the amount of trityl azide produced initially by the amount produced at infinity and subtracting from 1. In this example the amount of ester produced initially is 9.7%.

The calculation may also be based on the concentration of trityl perchlorate used and this serves as a cross check on the above procedure. The trityl perchlorate used for this series of experiments was found by two independent methods to be $85.0 \pm 0.6\%$ pure. From the weight of trityl perchlorate and its known purity a theoretical concentration of trityl azide of 2.878 mg/ml could be obtained. This value is identical with that observed by infrared measurements as the maximum amount of trityl azide produced at "infinity".

Quantitative Analysis of Trityl Perchlorate :

Procedure A:

Trityl perchlorate (0.2698 g., 0.03470 M) was weighed in a 25 ml volumetric flask and purified acetonitrile added to the mark. Using an automatic pipette 5 ml. aliquots of the above solution were transferred to 50 ml. Erlenmeyer flasks and 25 ml. of water added. The perchloric acid thus produced was titrated for with a standard solution of sodium methoxide with phenolphthalein as indicator. The results showed that 3.538 ± 0.001 ml. of sodium methoxide (0.04202 M) was needed to neutralize the acid produced. The amount of acid produced is 85.5% based on the theoretical amount of trityl perchlorate used.

Procedure B:

Tetrabutylammonium azide (0.1729 g., 0.06077 M) and trityl perchlorate (0.1174 g., 0.03572 M) were weighed in a 10 ml. volumetric flask and acetonitrile added to the mark. With the aid of an automatic pipette 5 ml of the above solution was added to a 10 ml. volumetric flask and acetonitrile added to the mark. In a manner previously described the region 2200 - 2100 cm^{-1} was scanned in the infrared and the absorbance at 2100 cm^{-1} due to trityl azide determined. From the absorbance value the concentration of trityl azide produced was found from the plot of concentration against absorbance. The absorbance value found in this example was 0.63895, and this is equivalent to 4.30 mg/ml of trityl azide. From the concentration of trityl perchlorate used originally the theoretical amount of trityl azide is 5.095 mg/ml. The percentage trityl azide produced of the theoretical is 84.4%, which value is identical within experimental error to that obtained by titrimetry as the percentage purity of trityl perchlorate.

CHAPTER III

The Reaction of Trityl 2,6-dimethylbenzenesulfinate with tetrabutylammonium salts in acetonitrile

In this chapter the results of the reaction of trityl 2,6-dimethylbenzenesulfinate, with tetra-n-butylammonium azide, 2-methylbenzenesulfinate, perchlorate and 2,6-dimethylbenzenesulfinate in acetonitrile are presented. The consequences of these results in the light of the detailed mechanism of the sulfinate-sulfone rearrangement are discussed.

RESULTS

The syntheses of the substrate and the reaction products have been presented previously. The kinetic procedure outlined in Chapter II for following the appearance of the trityl azide band at 2100 cm^{-1} , was the same as used here. The relationship between optical density and concentration for trityl azide at 2100 cm^{-1} was given in Chapter II (Figure XII, Table XIV).

A summary of the results of the reaction of trityl 2,6-dimethylbenzenesulfinate with tetrabutylammonium azide, 2-methylbenzenesulfinate, 2,6-dimethylbenzenesulfinate and perchlorate salts is given in Table XXX. All the rates listed in this table except runs 4-32 and 4-36 were calculated from measurements conducted in the infrared region $2200 - 2000\text{ cm}^{-1}$. Runs 4-32 and 4-36 involved measurements conducted in the ultraviolet at 305 mμ. The details will be presented later.

TABLE XXX

THE REACTION OF TRITYL 2,6-DIMETHYLBENZENESULFINATE WITH TETRABUTYLAMMONIUM
SALTS IN ACETONITRILE AT $25.23 \pm 24^{\circ(a)}$

Run	(Ester) M	(N ₃ ⁻) M	(2-salt) M	(2,6-salt) M	(ClO ₄ ⁻) M	k ₁ x 10 ⁵ sec ⁻¹
3-204	0.02247	0.06358	-	-	-	7.35 ^c 7.41 ± .44
3-206	.01959	"	-	-	-	7.66 ^c 8.07 ± .45
4-32 ^b	.01053	0.06540	-	-	-	7.55 ^c 7.62 ± .12
4-36 ^b	.01016	"	-	-	0.10603	7.40 ^c 7.57 ± .18
4-84	.02681	0.07299	-	-	.20952	7.20 ^c 7.26 ± .23
4-80	.02288	"	-	-	.20364	7.13 ^c 6.95 ± .55
3-210	.02439	0.06358	0.11032	-	-	7.66 ^c 7.42 ± .55
3-202	.02014	.06358	.10941	-	-	7.75 ^c 7.63 ± .39
3-194	.02329	"	.10714	-	-	7.60 ^c 7.27 ± .48
4-86	.02400	0.06102	-	0.10653	-	4.22 ^c 4.13 ± .21
4-82	.02482	.06202	-	.10630	-	4.20 ^c 4.28 ± .13
4-76	.02085	"	-	.21758	-	3.25 ^c 3.37 ± .30
4-78	.03122	"	-	.24380	-	2.78 ^c 2.79 ± .30

a-The temperature recorded here is the actual temperature of the reaction solution. The cell containing the reactants was stored in a Barnes Engineering Model 104 sealed cell thermostated at 25°. The temperature of the cell solution was obtained with the aid of a copper-constantan thermocouple.

b-Measured in the ultraviolet at 305 mμ.

c-Calculated from plot log (C_∞ - C) against time using initial slopes.

The reaction of trityl 2,6-dimethylbenzenesulfinate with tetrabutylammonium azide in acetonitrile did not give rise to good first-order kinetics. There is a definite downward drift apparent in the calculated first-order rate constants as the reaction progresses. Duplicate runs are reproducible within experimental error, but the average deviations are between 6 and 8% (Table XXX, run 3-204, 3-206). Under these conditions trityl azide is produced in quantitative yield. In run 3-204 and 3-206 100 and 99% trityl azide were produced respectively. A sample rate, run 3-204, is given in Table XXXI. A plot of $\log (C_{\infty} - C)$ against time for this rate is given in Figure XVIII. A reasonable straight line is obtained with the exception of one point. This point represents ca. 88% of reaction.

In the reaction of trityl 2,6-dimethylbenzenesulfinate with tetrabutylammonium azide and 2-methylbenzenesulfinate in acetonitrile good first-order kinetics were not observed. A downward drift is apparent in the first-order rate constants. The addition of tetrabutylammonium 2-methylbenzenesulfinate had no effect on the rate of disappearance of the ester. (Compare runs 3-204, 3-206, and 4-32 with runs 3-210, 3-202, 3-194 of Table XXX). The rate constants reported are the same within experimental error. Table XXXII shows a sample rate calculation and Figure XIX presents a plot of $\log (C_{\infty} - C)$ against time. Run 3-202 is used here as an example.

The reaction of trityl 2,6-dimethylbenzenesulfinate with tetrabutylammonium azide in the presence or absence of salts like tetrabutylammonium 2,6-dimethylbenzenesulfinate and perchlorate yields

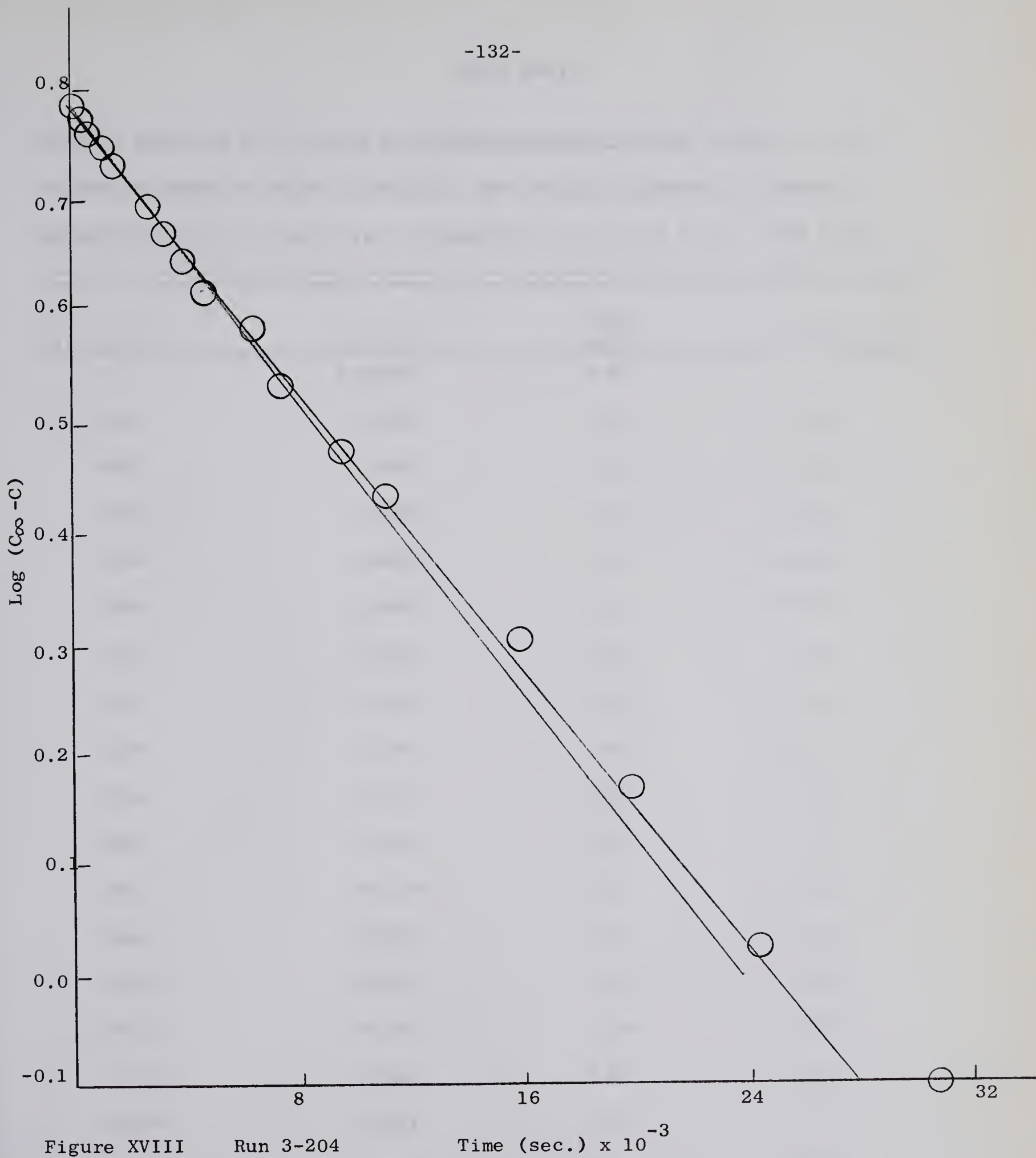
TABLE XXXI

RATE DATA OF REACTION OF TRITYL 2,6-DIMETHYLBENZENESULFINATE (0.0224 M)
WITH TETRABUTYLAMMONIUM AZIDE (0.06358 M) IN ACETONITRILE AT 25.23 \pm
0.24 $^{\circ}$ RUN 3-204

Time (sec.)	Log I ₀ /I	Cob. mg/ml	k x 10 ⁵ sec ⁻¹
0	0.05508	0.30	-
297	.08472	.47	-
619 ^(a)	.11462	.63	-
1021	.14747	.84	(9.21)
1427	.17532	1.10	8.40
2039	.22634	1.31	(8.80)
2573	.26532	1.54	7.75
3332	.29689	1.72	7.81
3935	.33519	1.95	7.77
4725	.37534	2.25	8.01
6468	.41581	2.53	6.83
7479	.47870	2.98	7.61
9596	.53723	3.41	7.33
11135	.57139	3.70	7.21
15872	.64449	4.40	7.00
19899	.69389	4.93	7.00
24543	.73395	5.35	7.12
30808	.74954	5.60	6.55
100320	.82225	6.40	Avg = 7.41 \pm .44 ^(b)

(a) - Taken as zero time in rate calculations.

(b) - k (from slope Figure XVIII) = 7.35×10^{-5} sec⁻¹



Relationship between $\log (C_{\infty} - C)$ against time for the reaction of trityl 2,6-dimethylbenzenesulfinate with azide ion in acetonitrile.

TABLE XXXII

RATE OF REACTION OF TRITYL 2,6-DIMETHYLBENZENESULFINATE (0.02014 M) WITH
TETRABUTYLAMMONIUM AZIDE (0.06358 M) AND TETRABUTYLAMMONIUM 2-METHYL-
BENZENESULFINATE (0.10941 M) IN ACETONITRILE AT $25.23 \pm .25^{\circ}$ RUN 3-202

Time (sec.)	Log I ₀ /I	Cob mg/ml	k x 10 ⁵ sec. ⁻¹
0	0.05346	0.30	-
525	.08666	.46	7.89
965	.10949	.59	7.89
1509	.13408	.75	8.01
2098	.16477	.95	(8.65)
2640	.19064	1.10	(8.55)
3383	.21944	1.26	8.22
4087	.24955	1.45	8.41
4929	.27686	1.60	8.11
6018	.30153	1.75	7.63
7066	.33212	1.93	7.54
7944	.35119	2.07	7.66
9484	.38437	2.30	7.45
10772	.40340	2.42	7.15
12423	.42352	2.58	6.93
15139	.46443	2.88	7.00
17038	.48561	3.05	6.97
20871	.50793	3.19	(6.29)
95131	.62666	4.25	Avg = 7.36 \pm .40
151981	.62741	4.25	

Cob. at infinity = 74% trityl azide of theoretical.

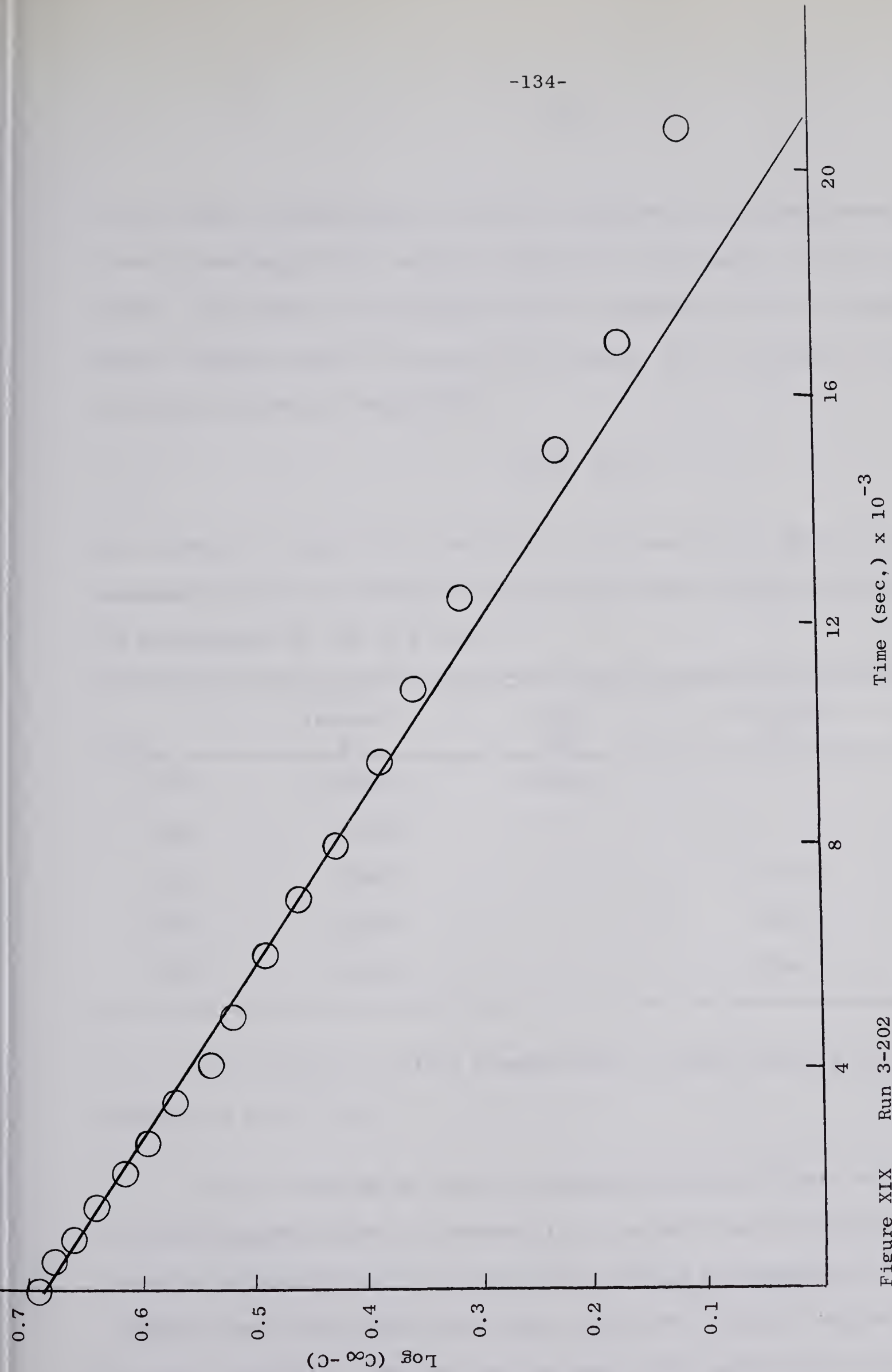


Figure XIX Run 3-202

Relationship between $\log(C_{\infty} - C)$ and time for the reaction of trityl 2,6-dimethylbenzenesulfinate with azide ion and added 2-methylbenzenesulfinate ion in acetonitrile at 25° .

trityl azide in quantitative yield. The addition of tetrabutylammonium 2-methylbenzenesulfinate caused a reduction in the amount of trityl azide formed. This result is consistent with the formation of trityl 2-methylphenyl sulfone as one of the reaction products (55). A summary of these findings is shown in Table XXXIII.

TABLE XXXIII

THE FRACTION OF TRITYL AZIDE PRODUCED IN THE REACTION OF TRITYL 2,6-DIMETHYLBENZENESULFINATE WITH TETRABUTYLAMMONIUM AZIDE AND 2-METHYLBENZENESULFINATE IN ACETONITRILE AT $25.23 \pm 0.24^{\circ}$.

Run	(Ester) M	(N_3^-) M	(2-salt) M	F _{azide}
3-204	0.02247	0.06358	-	1.00
3-206	.01959	"	-	0.99
3-210	.02439	"	0.11032	.75
3-194	.02329	"	.10714	.71
3-202	.02014	"	.10941	.74

The fraction of trityl 2-methylphenyl sulfone produced in the above examples is 0.27 ± 0.02 .

In the reaction of trityl 2,6-dimethylbenzenesulfinate with tetrabutylammonium azide in acetonitrile, the addition of tetrabutylammonium perchlorate had no effect on the rate of disappearance of ester, (Compare runs 3-204, 3-206, 4-32 with runs 4-36, 4-84 and 4-80 of Table XXX). The rate constants observed are the same within experimental error.

There is no drift apparent in the first-order rate constants as the reaction progresses. The addition of the perchlorate salt had no effect on the fraction of trityl azide produced. Table XXXIV shows a sample rate calculation representing run 4-84. Figure XX shows a plot of $\log (C_{\infty} - C)$ against time. A reasonable straight line is obtained. Duplicate runs 4-84 and 4-80 of Table XXX, are reproducible within experimental error.

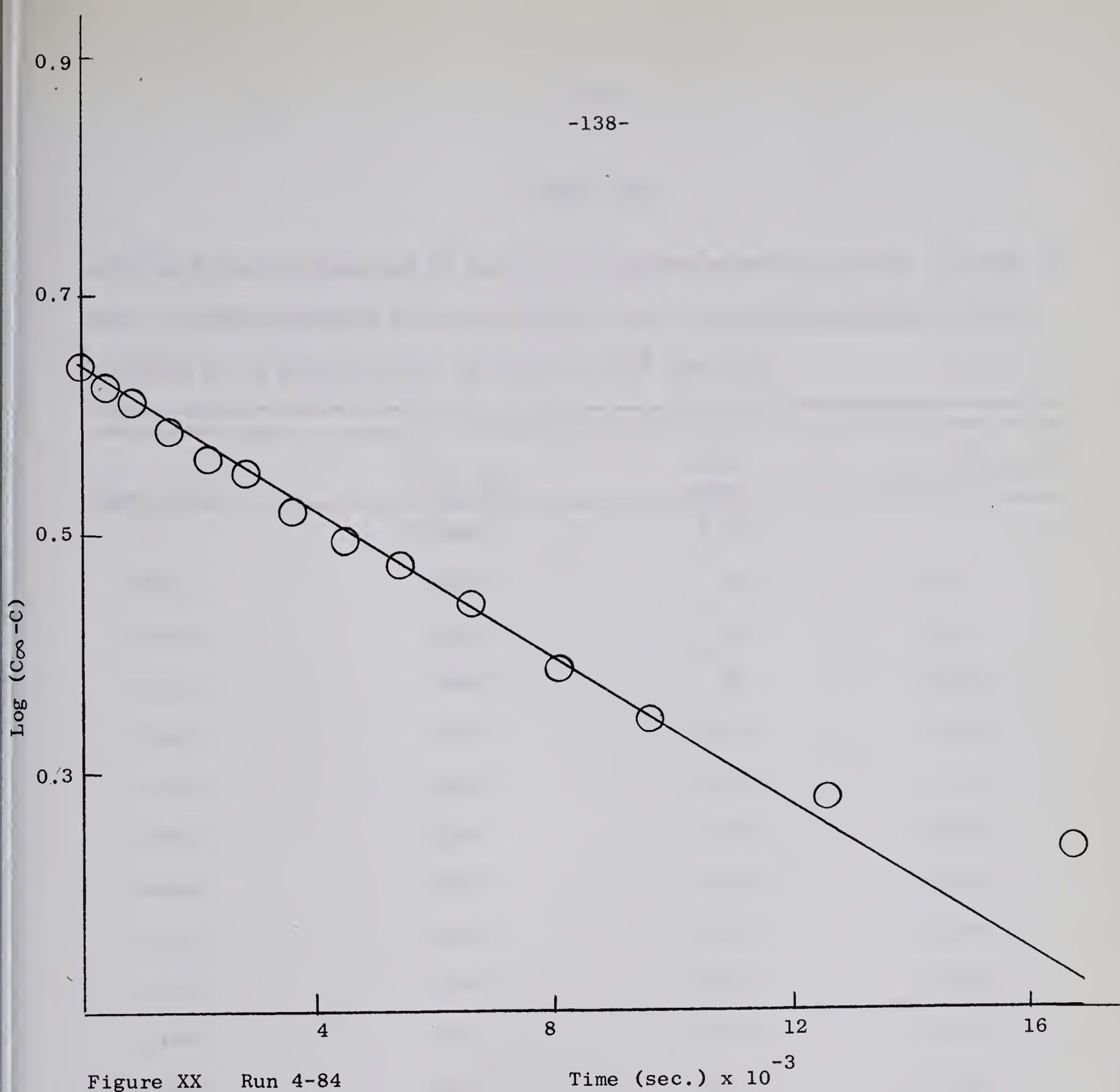
When trityl 2,6-dimethylbenzenesulfinate is allowed to react with tetrabutylammonium azide in acetonitrile in the presence of 0.11 M tetrabutylammonium 2,6-dimethylbenzenesulfinate ca. 40 - 45% depression in the first-order rate constant was observed. The addition of higher concentrations of salt resulted in further depressions of the rate constants. In one instance good first-order kinetics were obtained with no apparent drift in the observed first-order rate constants. In this case the average deviation is within 4%. In another instance there is a downward drift associated with the first-order rate constants. The average deviation in this case is about 9%. The addition of tetrabutylammonium 2,6-dimethylbenzenesulfinate had no effect on the fraction of trityl azide produced. A summary of these results is given in Table XXX, (runs 4-86, 4-82, 4-76 and 4-78). Duplicate runs 4-86 and 4-82 are reproducible within experimental error. A sample rate calculation is presented in Table XXXV for run 4-82. This determination involved a tetrabutylammonium 2,6-dimethylbenzenesulfinate concentration of 0.11 M. Figure XXI shows a plot of $\log (C_{\infty} - C)$ against time. Table XXXVI presents a sample rate for run 4-76. This rate involved

TABLE XXXIV

RATE DATA FOR THE REACTION OF TRITYL 2,6-DIMETHYLBENZENESULFINATE (0.02681 M) WITH TETRABUTYLAMMONIUM AZIDE (0.07299 M) AND PERCHLORATE (0.20952 M) IN ACETONITRILE AT $25.23 \pm 0.24^{\circ}$ RUN 4-84

Time (sec.)	Log I ₀ /I	Cob mg/ml	$k_1 \times 10^5 \text{ sec.}^{-1}$
0	0.0481	0.28	-
281	.0931	.53	-
685 ^(a)	.1383	.80	-
1172	.1741	1.01	(6.38)
1628	.2165	1.26	7.31
2244	.2707	1.58	7.70
2828	.3101	1.80	(7.95)
3469	.3522	2.06	7.25
4249	.4081	2.45	7.68
5134	.4490	2.75	7.47
6050	.4803	2.98	7.11
7253	.5261	3.33	6.98
8753	.5874	3.83	7.18
10189	.6297	4.22	7.24
13138	.6728	4.69	6.68
17259	.7028	4.96	(5.59)
96720	.8696	7.54	Avg = $7.26 \pm .23$
139058	.8809	7.75	
160695	.8617	7.40	

(a) - Used as zero time in the rate calculation.



The relationship between $\log (C_{\infty} - C)$ and time for the reaction of trityl 2,6-dimethylbenzenesulfinate with tetrabutylammonium azide and perchlorate in acetonitrile at 25° .

TABLE XXXV

RATE DATA FOR THE REACTION OF TRITYL 2,6-DIMETHYLBENZENESULFINATE (0.02482 M)
WITH TETRABUTYLAMMONIUM AZIDE (0.07299 M) AND 2,6-DIMETHYLBENZENESULFINATE
(0.10630 M) IN ACETONITRILE AT $25.23 \pm 0.24^{\circ}$ RUN 4-82

Time (sec.)	Log I ₀ /I	Cob mg/ml	$k_1 \times 10^5 \text{ sec.}^{-1}$
0	0.0539	0.30	-
485	.0759	.45	4.60
1096	.1048	.61	4.27
1870	.1486	.87	4.68
2487	.1773	1.03	4.55
3149	.1998	1.17	4.34
3873	.2495	1.46	(4.84)
4426	.2620	1.52	4.47
5411	.2949	1.72	4.36
6575	.3383	1.97	4.29
7186	.3631	2.15	4.42
10281	.4374	2.67	4.16
12596	.4839	3.00	4.02
16140	.5452	3.47	(3.89)
14456	.6193	4.11	4.21
28375	.7137	5.09	4.28
126944	.8491	7.10	Avg. $k_1 = 4.28 \pm 0.13$
172776	.8491	7.10	

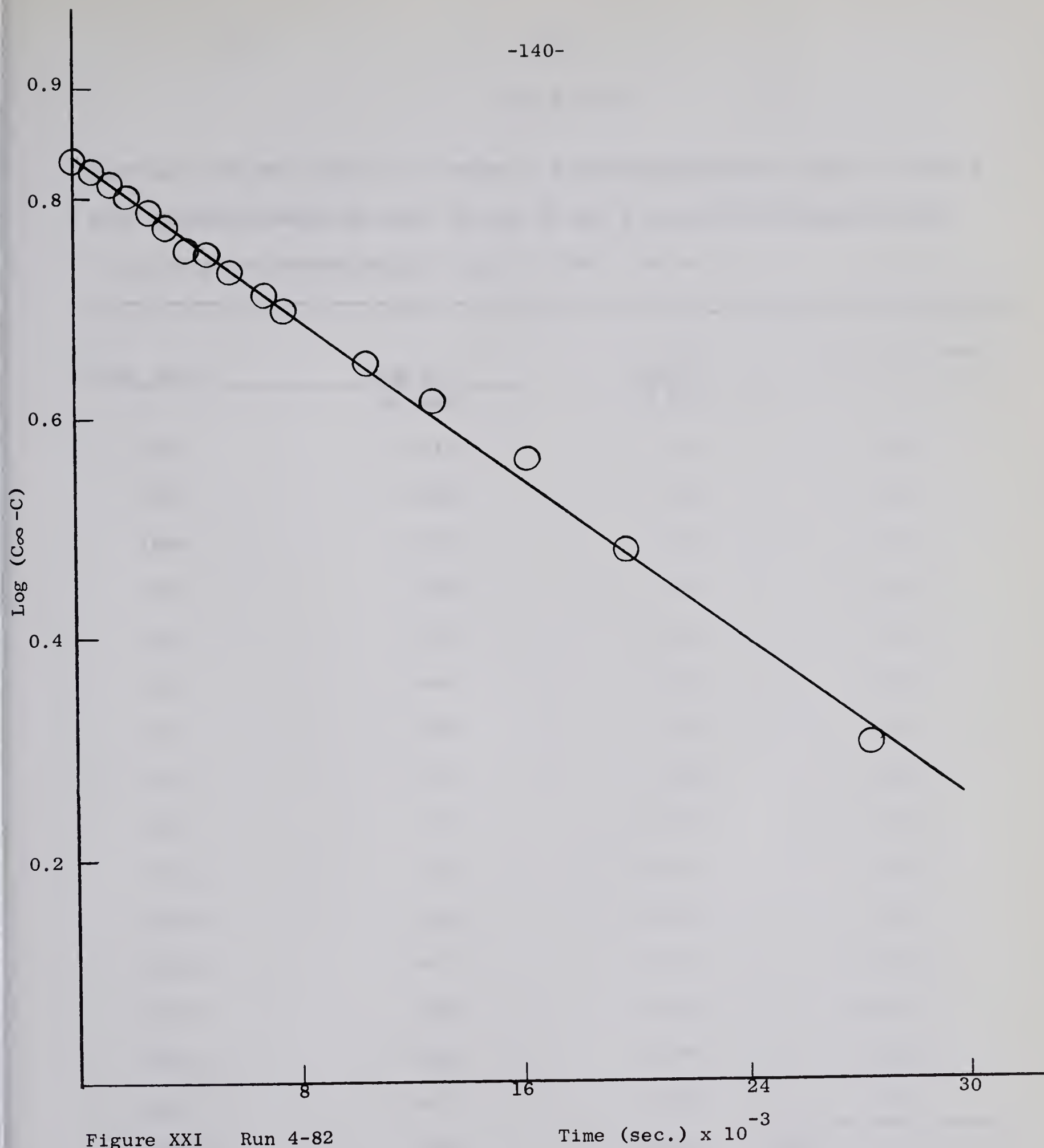


Figure XXI Run 4-82

Relationship between $\log (C_{\infty} - C)$ and time for the reaction of trityl 2,6-dimethylbenzenesulfinate with tetrabutylammonium azide and 2,6-dimethylbenzenesulfinate in acetonitrile at 25° .

TABLE XXXVI

RATE DATA FOR THE REACTION OF TRITYL 2,6-DIMETHYLBENZENESULFINATE (0.02085 M)
WITH TETRABUTYLAMMONIUM AZIDE (0.0730 M) AND 2,6-DIMETHYLBENZENESULFINATE
(0.21758 M) IN ACETONITRILE AT $25.23 \pm 0.24^{\circ}$ RUN 4-76

Time (sec.)	Log I ₀ /I	Cob mg/ml	$k_1 \times 10^5 \text{ sec.}^{-1}$
0	0.0453	0.25	-
468	.0618	.35	3.87
1070	.0842	.48	3.93
1898	.1113	.59	3.34
2917	.1584	.92	(4.39)
4127	.1858	1.08	3.90
5021	.1940	1.12	3.38
9194	.2955	1.73	3.37
11100	.3391	1.94	3.25
12991	.3701	2.19	3.30
16206	.3915	2.34	2.92
17726	.4088	2.45	2.84
22989	.4012	2.40	(2.13)
28386	.4726	2.92	(2.13)
59396	.5808	3.77	(1.69)
62037	.6921	4.82	2.95
259005	.7562	5.61	Avg = 3.37 ± 0.30
321927	.7718	5.81	
544093	.7718	5.81	

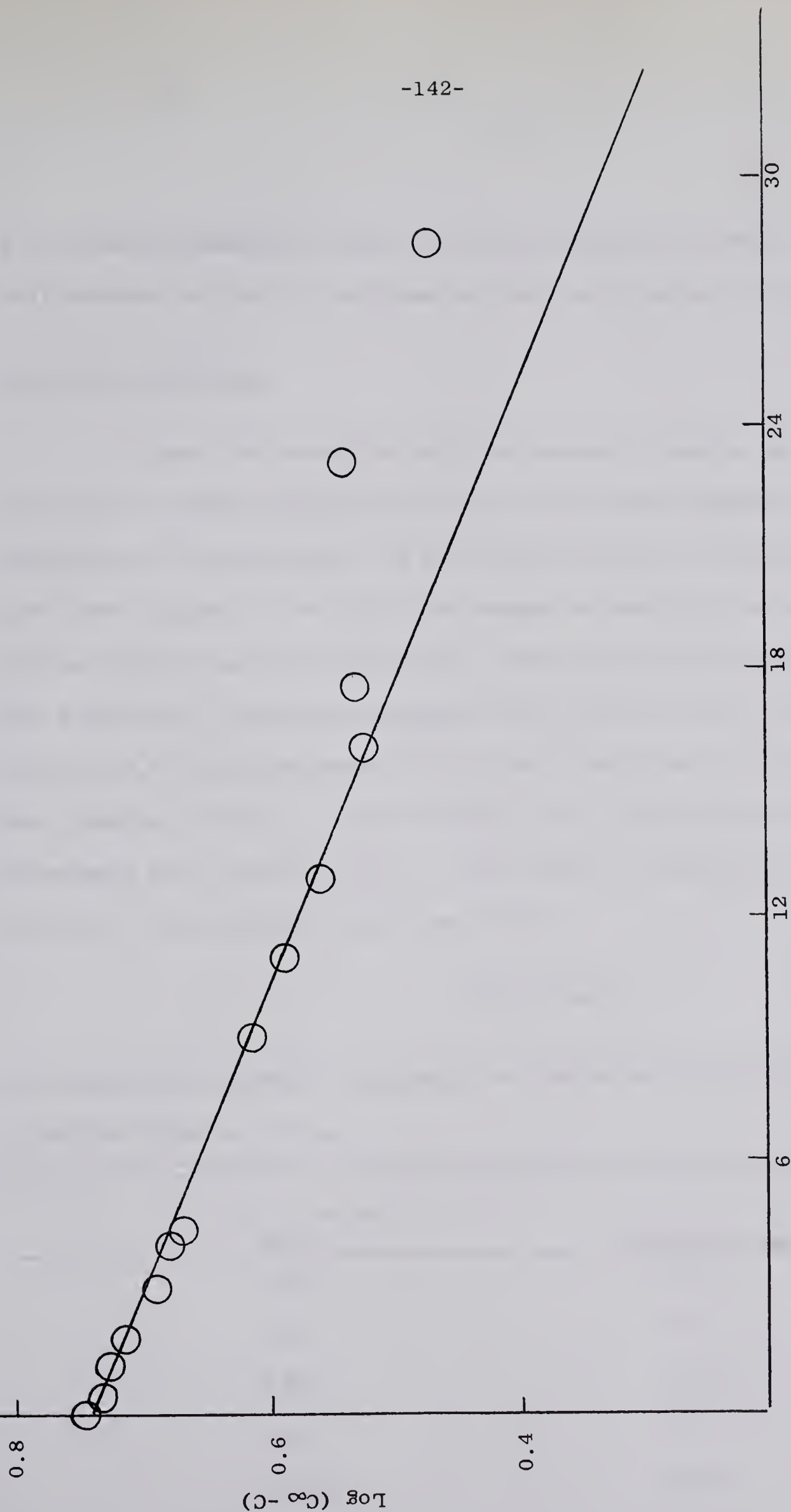


Figure XXII Run 4-76 Time (sec.) $\times 10^{-3}$

The relationship between $\log (C_{\infty} - C)$ and time for the reaction of trityl 2,6-dimethylbenzenesulfinate with tetrabutylammonium azide and 2,6-dimethylbenzenesulfinate in acetonitrile at 25° .

a 2,6-dimethylbenzenesulfinate salt concentration of 0.22 M. The relationship between $\log (C_{\infty} - C)$ and time for this run is given in Figure XXII.

Rate data at 305 mu.

In Table XXX runs 4-32 and 4-36 summarize results of the reaction of trityl 2,6-dimethylbenzenesulfinate with tetrabutylammonium azide and perchlorate in acetonitrile. In these runs the rate of disappearance of ester was followed by recording the change in absorbance with time at 305 mu which is due to trityl azide. Trityl 2,6-dimethylbenzenesulfinate has a small but observable absorbance ($\epsilon = 16$) at 305 mu. Tetrabutylammonium 2,6-dimethylbenzenesulfinate the other product of the reaction also absorbs ($\epsilon = 30$) at this wavelength. The relationship between absorbance and concentration for trityl azide in acetonitrile at 305 mu is shown in Table XXXVII and Figure XXIII.

TABLE XXXVII

THE RELATIONSHIP BETWEEN ABSORBANCE AND CONCENTRATION FOR TRITYL AZIDE IN ACETONITRILE AT 305 mu.

10 x (Trityl Azide) mg/ml	Absorbance
4.014	0.431
3.211	.353
2.007	.228
1.004	.116
0.5018	.058

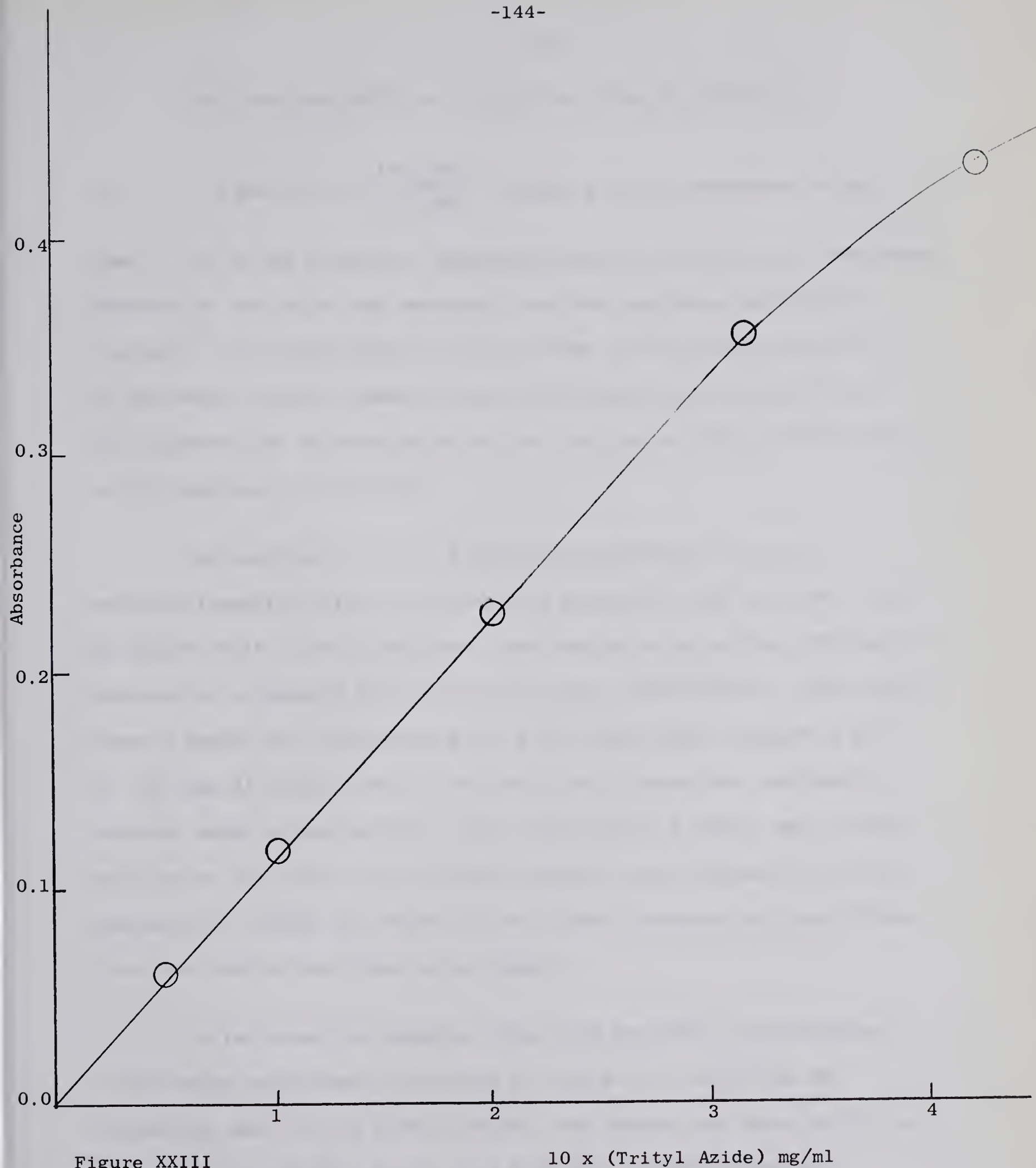


Figure XXIII

10 x (Trityl Azide) mg/ml

The relationship between optical density and concentration for trityl azide in acetonitrile at 305 mμ.

The rate constants were calculated from the equation :

$$kt = 2.303 \log \frac{(A_{\infty} - A_0)}{(A_{\infty} - A)} \quad \text{where } A \text{ is the absorbance at any}$$

time t , A_0 is the absorbance observed initially, and A_{∞} is the absorbance observed at the end of the reaction. From the absorbance observed at "infinity" the concentration of trityl azide is obtained from the plot of absorbance against concentration. By dividing this concentration by the concentration of starting ester the fraction of trityl azide produced in the reaction is determined.

The reaction of trityl 2,6-dimethylbenzenesulfinate with tetrabutylammonium azide in acetonitrile measured at 305 μ showed first an upward drift in the first-order rate constants up to about 20% reaction, followed by a downward drift starting at about 72% reaction. Table XXXVIII shows a sample rate representing run 4-32. Figure XXIV presents a plot of $\log (A_{\infty} - A)$ versus time for the reaction of ester with tetrabutylammonium azide in acetonitrile. Table XXXIX shows a sample rate for the reaction of the ester with tetrabutylammonium azide and perchlorate in acetonitrile. Figure XXV shows the relationship between $\log (A_{\infty} - A)$ and time. Run 4-36 is used here as an example.

In the above two examples (runs 4-32 and 4-36) the percentage trityl azide calculated at infinity for run 4-32 is 106.5% of the theoretical and for run 4-36 is 104.5%. The reason that these infinities are greater than 100% is due to the fact that tetrabutylammonium 2,6-dimethylbenzenesulfinate has a small but observable absorbance at

TABLE XXXVIII

RATE OF REACTION OF TRITYL 2,6-DIMETHYLBENZENESULFINATE (1.0534×10^{-3} M)
 WITH TETRABUTYLAMMONIUM AZIDE (0.06540 M) IN ACETONITRILE AT 305 mu AT
 $25.15 \pm 0.15^{\circ}$ RUN 4-32

Time (sec.)	Absorbance	$k \times 10^5 \text{ sec.}^{-1}$
0	0.016	-
160 ^(b)	.024	-
647	.036	(6.88)
1370	.051	(6.55)
1939	.063	(6.60)
2441	.075	(6.85)
2660	.086	7.80
3340	.098	7.45
3880	.107	7.30
4471	.120	7.50
5035	.131	7.56
5773	.145	7.65
6320	.155	7.67
7300	.170	7.64
8342	.186	7.68
10191	.207	7.73
11510	.225	7.64
11790	.232	7.86
17421	.264	(6.85)
23832	.301	(6.80)
89040	.369	Avg = 7.62 ± 0.12 ^(a)

(a) - Rate constants indicated in brackets were omitted in calculating this (average)

(b) - Used as zero time in the rate calculation.

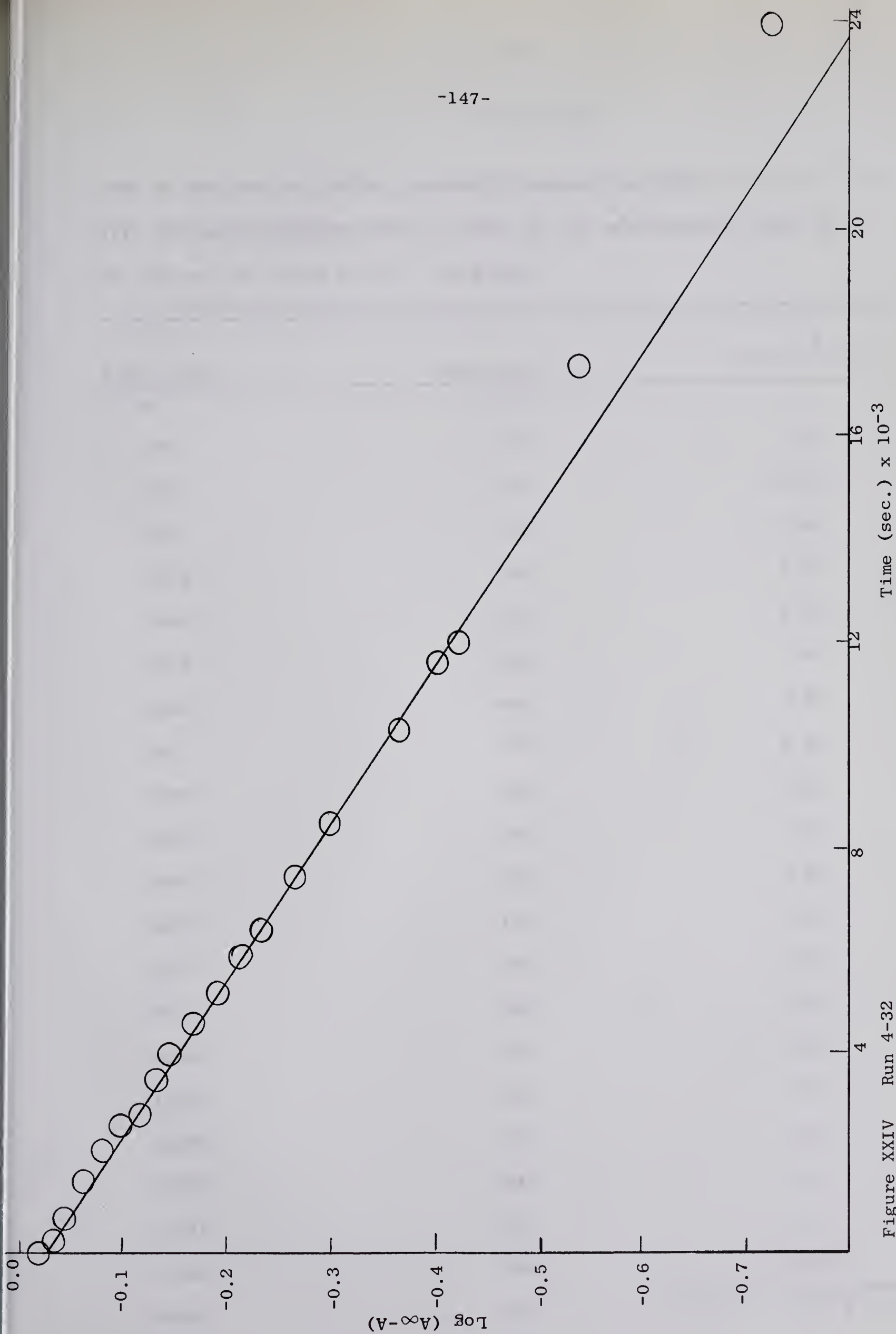


Figure XXIV Run 4-32

The relationship between $\log (A_{\infty} - A)$ and time for the reaction of trityl 2,6-dimethylbenzene-sulfonate and azide salt in acetonitrile at 25° .

TABLE XXXIX

RATE OF REACTION OF TRITYL 2,6-DIMETHYLBENZENESULFINATE (1.016×10^{-3} M)
 WITH TETRABUTYLAMMONIUM AZIDE (0.06540 M) AND PERCHLORATE (0.10603 M)
 AT 305 mμ AT $25.15 \pm 0.15^{\circ}$ RUN 4-36

Time (sec.)	Absorbance	$k_1 \times 10^5 \text{ sec.}^{-1}$
0	0.045	-
88	.047	7.85
218	.050	(8.50)
440	.055	7.66
1118	.070	7.50
1493	.078	7.73
2176	.090	7.38
2728	.099	7.22
3311	.107	8.00
3499	.120	8.00
4451	.132	7.60
5050	.142	7.62
5970	.157	7.70
7310	.174	7.60
9795	.199	7.50
10520	.207	7.45
11052	.214	7.38
12798	.228	7.22
15375	.249	7.28
17211	.253	(6.72)
21220	.290	(6.68)
90420	.349	Avg. = 7.57 ± 0.18
109320	.350	

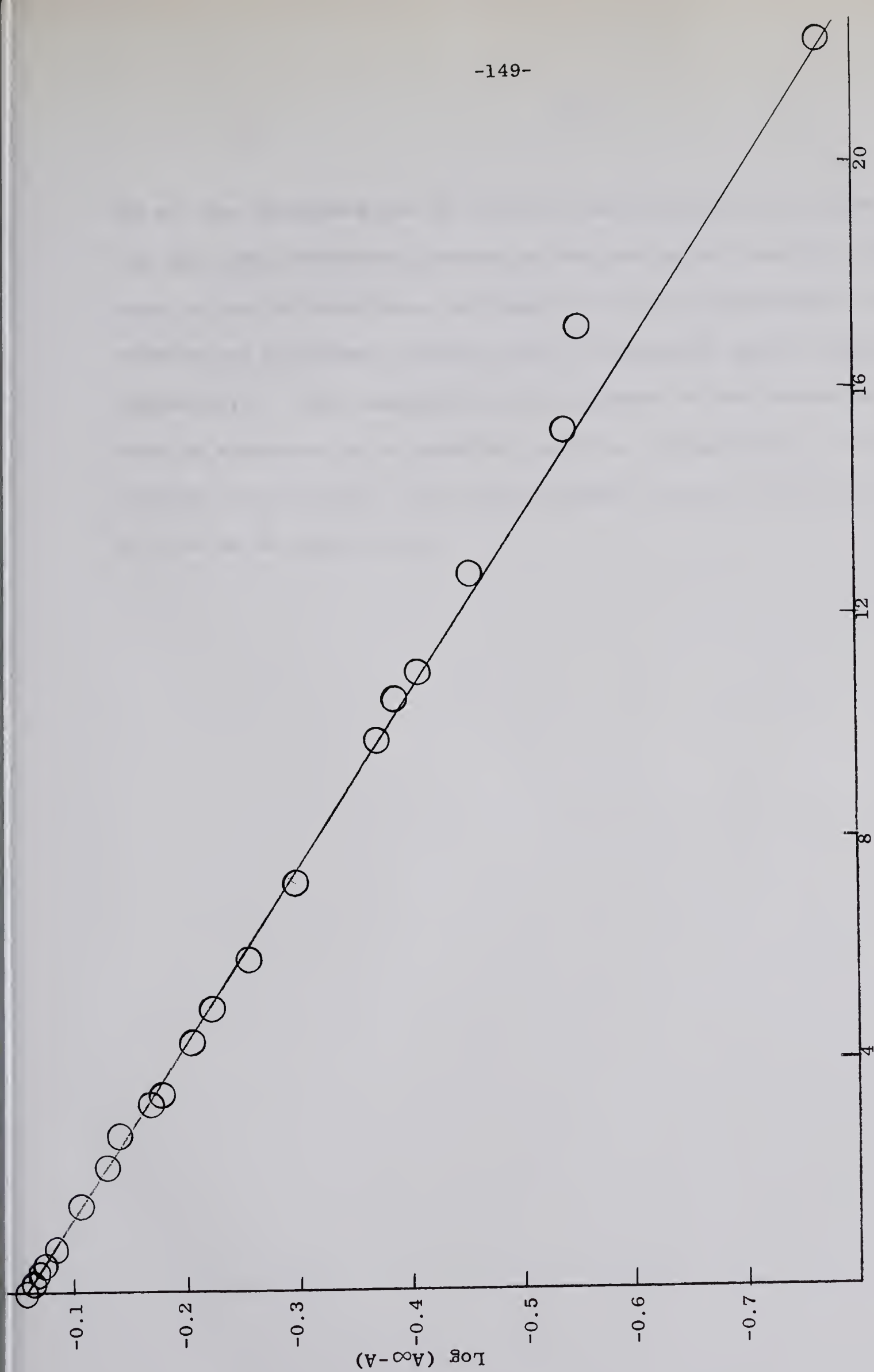


Figure XXV Run 4-36

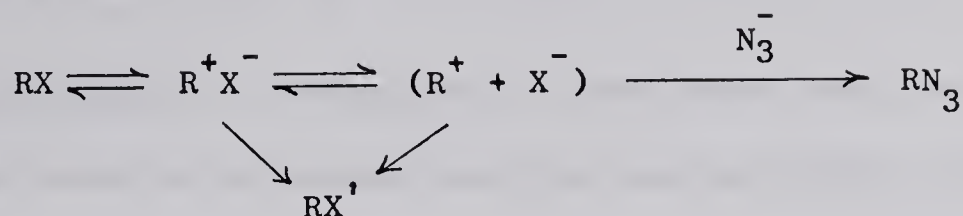
The relationship between $\log (A_{\infty} - A)$ and time for the reaction of trityl 2,6-dimethylbenzenesulfonate with tetrabutylammonium azide and perchlorate in acetonitrile at 25^o.

305 mu. The absorbance due to this salt was determined and subtracted from the total absorbance observed at the end of the reaction. From the value of the new absorbance the amount of trityl azide produced in the reaction was determined from the plot of absorbance against concentration (Figure XXII). This concentration was compared to the concentration of starting substrate and a corrected value for the percentage trityl azide produced was determined. The values obtained for runs 4-32 and 4-36 are 97.0 and 96.6% respectively.

DISCUSSION

Consider the following scheme :

SCHEME I

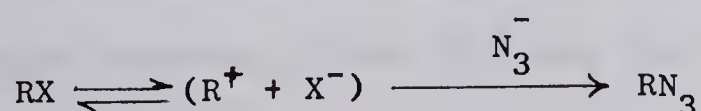


In the case where RX is trityl 2-methylbenzenesulfinate recombination of the intimate ion pair R^+X^- or the trappable species $(\text{R}^+ + \text{X}^-)$ can lead to the reformation of the substrate together with the formation of trityl 2-methylphenyl sulfone. This introduces difficulties into the system for studying the nature of the capturable species as was pointed out in Chapter II.

The fact that trityl 2,6-dimethylbenzenesulfinate does not rearrange to a sulfone (55) but does undergo exchange reactions makes this compound an ideal model for comparative study. This ester is perhaps the best available model for studying common ion rate depression, with the added assurance that sulfone formation would not complicate the results.

Consider Scheme I where RX is trityl 2,6-dimethylbenzenesulfinate. Ionization to produce the intimate ion pair R^+X^- will be followed by recombination of this species to regenerate the substrate or further separate to give $(\text{R}^+ + \text{X}^-)$ and will not give rearrangement to sulfone. In this case Scheme I can be simplified and be represented by Scheme II.

SCHEME II



In such a scheme if $(R^+ + X^-)$ were dissociated ions common ion rate depression may be detected, by addition of the common ion X^- and by measuring the extent of depression on the first-order rate constant.

In Chapter II (Table XXVI) it was shown that the 2,6-dimethylbenzenesulfinate anion recombines with the capturable trityl cationic species to give trityl 2,6-dimethylbenzenesulfinate. The azide/2,6-dimethylbenzenesulfinate competition factor observed is ca 10. This indicates that when equimolar concentrations of tetrabutylammonium azide and 2,6-dimethylbenzenesulfinate is employed the 2,6-dimethylbenzenesulfinate ion should capture at least 10% of the trappable carbonium ion intermediate. As the 2,6-dimethylbenzenesulfinate ion concentration is increased relative to azide ion, more and more capture by the sulfinate ion should occur to yield trityl 2,6-dimethylbenzenesulfinate. Therefore in the case of trityl 2,6-dimethylbenzenesulfinate common ion rate depression can be detected and measured if it occurs.

The results of the reaction of trityl 2,6-dimethylbenzenesulfinate with tetrabutylammonium azide in acetonitrile show that addition of 0.11 M tetrabutylammonium 2,6-dimethylbenzenesulfinate resulted in ca. a 40 - 45% depression of the first-order rate constant (Table XXX). Addition of higher concentrations of the common ion salt resulted in greater depressions in rate depending on the concentrations of tetrabutylammonium 2,6-dimethylbenzenesulfinate employed. The addition of tetrabutylammonium perchlorate had no effect on the rate of disappearance of the ester. The first-order rate constants observed (Table XXX) are the same within experimental

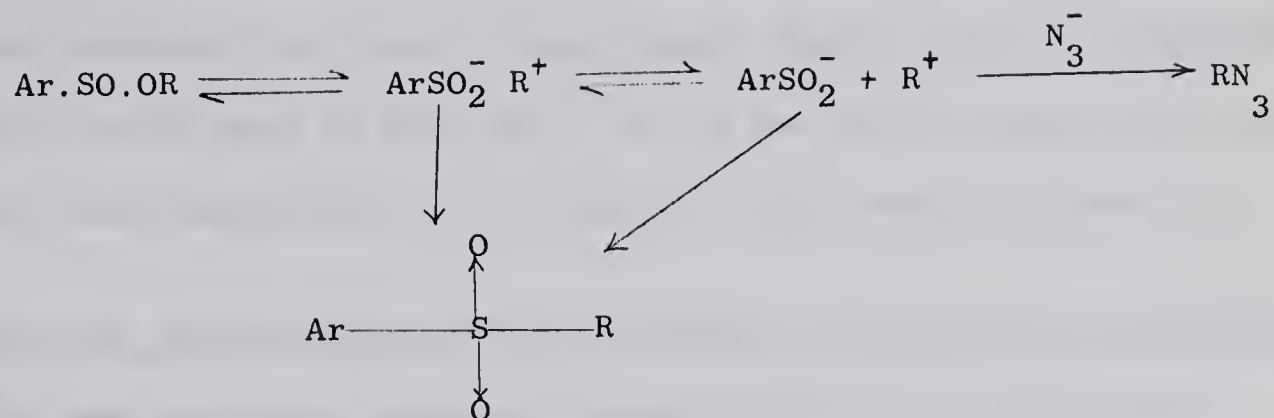
error as in the absence of this salt. Therefore the depression in rate is due to the 2,6-dimethylbenzenesulfinate ion, and is an example of common ion rate depression. This result is an unequivocal demonstration that dissociated ions are present under these reaction conditions. Therefore the species ($R^+ + X^-$) depicted in Scheme I and II must be dissociated ions.

From a consideration of the competition factor one would expect to a first approximation, ca. a 20% depression of the first-order rate constant when 0.061 M tetrabutylammonium azide and 0.11 M 2,6-dimethylbenzenesulfinate are employed. However a depression of twice this amount is observed. This may indicate that trityl perchlorate is not a perfect model for the capturable trityl cation generated by trityl 2,6-dimethylbenzenesulfinate. Since the competition experiments involve adding trityl perchlorate to a mixture of tetrabutylammonium azide and 2,6-dimethylbenzenesulfinate in acetonitrile, it is quite possible that under these conditions trityl perchlorate may not be reacting totally as dissociated ions. The discrepancy may also be due to some other factor or factors.

The close structural relationship between trityl 2-methylbenzenesulfinate and trityl 2,6-dimethylbenzenesulfinate suggests that both esters will undergo exchange reactions by an identical route under the same reaction conditions. That is, it is expected that both esters will generate the same type of capturable carbonium ion species. Therefore in the reaction of trityl 2-methylbenzenesulfinate with tetrabutylammonium azide in acetonitrile, dissociated ions must be the capturable species. It is felt that the concurrent rearrangement and substitution of this ester in acetonitrile

is best represented as in Scheme III.

SCHEME III



EXPERIMENTAL

Kinetic Measurements :

The procedure for kinetic measurements which follow the appearance of the trityl azide band at 2100 cm^{-1} , by the use of the Perkin Elmer Model 21 Infrared Spectrophotometer is the same as that used in Chapter II.

Lambert-Beer Law Determination of Trityl azide in Acetonitrile at 305 μ . :

The same procedure employed for determining the relationship between optical density and concentration for trityl 2-methylphenyl sulfone in acetonitrile at 283 μ , by the use of the Beckman DU Spectrophotometer was used to determine the relationship between optical density and concentration for trityl azide in acetonitrile at 305 μ .

Rate data at 305 μ :

The kinetic procedure used was identical to that used for following the trityl 2-methylphenyl sulfone absorbance at 283 μ by employing the Beckman DU Ultraviolet Spectrophotometer.

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